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STUDIES ON STRUCTURE AND
SYNTHESIS OF β -DICARBONYLS

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Preface

I should like to express my warmest gratitude to Professor Zen-ichi Yoshida who served as my research advisor during the course of this work. His kindly guidance and enthusiastic interest are sincerely appreciated. I am also indebted to Dr. Kazuo Nakamoto for permitting me to stay at Illinois Institute of Technology and for giving me the big chance to study the theory of vibrational spectrum. The author further wishes to express his sincere thanks to Dr. Robert Adams Condrate, Dr. Masaru Hojo, Dr. Shigeo Yoneda, Mr. Takao Tokumitsu and Mr. Yasutaka Shimizu who gave me suggestive discussions. The author's great thanks are due to Professor Yoshimasa Takezaki and Dr. Kenji Kanasaki for their continuous encouragement to him. Finally, I am very grateful to Mrs. Sadae Furukawa and Miss Keiko Mori for their typing this thesis and shall never forget their kindness.

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Introduction

Since the importance of the hydrogen bond in the chemical bond was recognized by Pauling, the phenomena of hydrogen bonding have been given considerable attention by chemists and physicists for almost forty years.¹⁻³ Even though so many works have been published to elucidate the nature of hydrogen bond, we are still lacking a great deal of the quantitative understanding. Further, the importance of the hydrogen bond associated with the energy transfer and the replication process will be increased in the field of the molecular biology and biochemistry.

In a last decade, the rapid progress in spectrophotometers enables us to approach to the micro-structure and dynamic properties of the hydrogen bond. Moreover, the development of large scale computer has offered facilities for mathematical treatment such as molecular orbital calculation and normal coordinate analysis.

Among recent physico-chemical methods, vibrational spectra have provided as the most powerful tools for the elucidation of the nature of the hydrogen bond. It should be noted, however, that previous vibrational studies have concentrated on the stretching band in the higher frequency region, and rather little information is reported for the lower frequency vibrations such as O-H·····O and bending of O-H·····O.

Further, the lower frequency appears in the region of far infrared, where one can not perform a correct assignment any more as in higher region according to the concept of the group vibrations. Consequently, the theoretical analysis of the vibrational spectra can be made in aid of normal coordinate analysis. This permits one to calculate the force constants which represent the magnitude of inter-atomic forces in molecule. If the force constants relating to O-H.....O system are obtained for a series of compounds, they can serve as a measure of the relative strength of the hydrogen bond.

Extensive investigations on tautomeric equilibrium of β -dicarbonyls have been carried out by organic and physical chemists. Nevertheless, there have never been reported for the comprehensive and conclusive works on intramolecular hydrogen bond itself of the enol form of β -dicarbonyls involving π -conjugative systems. Quasi aromatic properties of the chelate ring is of particular interest in view of structural chemistry and its reactivity. It is still pending problem whether the participation of vacant 2p-orbital of hydrogen can construct 6π -electrons system or not, as has been proposed by Shigorin.² Therefore, even though phenomena are familiar to us, attractive and challengeable problems to be solved have been accumulated in modern chemistry.

Chapter I is concerned with the study on the linear hydrogen

bond of acidic carbonate ion. Normal coordinate analysis has been carried out to analyse theoretically vibrational spectra using Urey-Bradley force field. It has been established that the resultant force constants in connection with the hydrogen bonding are correlated with the distance of $O \cdots O$. A nature of bend type hydrogen bond associated with π -conjugative system such as acetylacetone is quite different from that of linear hydrogen bond as has been introduced in the first chapter. Thus, in Chapter II, the author studies the theoretical treatment of the vibrational spectra of the enol form of β -diketones. The chemical shifts of enol proton of enol are coorelated with the chelated carbonyl stretching vibrations. This chapter includes the first observation of intramolecularly hydrogen bond stretching mode which is theoretically determined by the potential energy distribution.

Chapter III deals with the studies on the electronic effect of 3-substituents on the chelate ring of 2,4-pentanedione (acetylacetone). It has been proposed that the participation of vacant 2p-orbital of hydrogen atom is not necessary to explain electronic effect of substituents.

The marked $p\pi-d\pi$ conjugative stabilization of sulfur directly linked to the chelate ring and easier synthetic pathway with sulfur nucleophile are presented in Chapter IV. In Chapter V, the first succesful nucleophilic substitution reaction of trivalent metal

acetylacetonates has been reported. The reaction mechanism is interpreted considering the effect of solvents and substituents.

Chapter VI treats with cyclopropyl conjugation with the chelate ring in comparison with the corresponding iso-propyl substituted β -diketones at the both ground and electronically excited states. Its effect on the copper complexes of β -diketones is discussed in the same chapter.

In Chapter VII, the molecular orbital calculation of enolate ion of β -dicarbonyls in Hückel and Self-Consistent Field approximation has carried out in order to study the electronic structure which is strongly perturbed by intramolecular hydrogen bond.

In Chapter VIII, the theory of normal coordinate analysis is briefly introduced. Its application has been demonstrated for two highly enolized 3-substituted-2,4-pentanedione. Resultant force constants show good agreement with the results of nmr spectra.

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Chapter 1

Normal Coordinate Analysis of Hydrogen Bonded Compounds.

The Acid carbonate Ion*¹

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*1 Published in J. Chem. Phys., 43, 1177 (1965)

1.1 Summary

The infrared spectra of potassium acid carbonate and its deuterio analog have been obtained from 4000 to 160 cm^{-1} . The Raman spectrum of the latter has also been obtained in the crystalline state. A normal coordinate analysis has been carried out to estimate the force constants as well as to make theoretical band assignments. The infrared bands of the non-deuterated compound at 2620, 1405, and 248 cm^{-1} have been assigned to the O-H stretching, O-H·····O in-plane bending, and O·····H stretching coupled with C=O bending modes, respectively. The corresponding force constants are: O-H stretching, 3.20, O-H·····O bending, 0.22, and O·····H stretching, 0.76 mdyne/Å. Plots of these force constants versus O-H·····O distances for three compounds thus far investigated yield a linear relationship for each force constant.

1.2 Introduction

In previous papers of this series, we have reported normal coordinate analyses of acetic (and formic) acid dimer¹ and of the acid maleate ion²; the O-H·····O bond of the former is relatively long (2.74 Å), whereas that of the latter is extremely short (2.44 Å). It is, therefore, of particular interest to carry out a normal coordinate analysis of a hydrogen-bonded compound which has an O-H·····O bond of intermediate length, and to investigate the variation of force constants

as a function of the O-H.....O distance. According to the results of an x-ray analysis,³ the acid carbonate ion in KHCO_3 is dimerized through O-H.....O bonds 2.61 Å long, to form a ring structure similar to that of acetic acid dimer. Therefore, crystalline potassium acid carbonate serves as an ideal compound for this study.

The infrared spectra of KHCO_3 and KDCO_3 have been studied by Tarte,⁴ Ryskin,⁵ and Novak et al.⁶ Among these, the last investigators have made the most complete band assignments in the NaCl region. However, no infrared spectra have yet been obtained below 600 cm^{-1} where the O.....H stretching and ring deformation modes may appear. The Raman spectrum of crystalline KHCO_3 has been obtained by Couture-Mathieu.^{7,8} No Raman data, however, are yet available for crystalline KDCO_3 .

In this paper, we report the infrared spectra of KHCO_3 and KDCO_3 from 4000 to 160 cm^{-1} and the Raman spectrum of the latter in the crystalline state. We also describe the results of a normal coordinate analysis of the acid carbonate ion, and discuss the force constants of the O-H.....O system in connection with our previous papers.^{1,2}

1.3 Experimental

Preparation of Compounds

Potassium acid carbonate (KHCO_3) was purchased from Fisher Scientific Company, Chicago, and recrystallized from aqueous solution by passing in CO_2 gas below 70°C . KDCO_3 was obtained by dissolving crystalline K_2CO_3 in D_2O and passing in CO_2 gas. Both compounds were dried in an atmosphere of CO_2 .

Spectral Measurements

The infrared spectra were obtained by using a Perkin-Elmer Model 21 infrared spectrophotometer ($4000\text{--}650\text{ cm}^{-1}$), a Beckman Model IR 7 infrared spectrophotometer equipped with CsI optics ($700\text{--}250\text{ cm}^{-1}$), and a Perkin-Elmer Model 301 far-infrared spectrophotometer ($320\text{--}160\text{ cm}^{-1}$). The KBr-disk method was employed for the range between 4000 and 650 cm^{-1} , whereas the Nujol mull technique was used with CsI and polyethylene windows for the ranges between 700 and 250 cm^{-1} and between 320 and 160 cm^{-1} , respectively.

The Raman spectrum of KDCO_3 was obtained by using a Cary Model 81 Raman spectrometer with a single crystal of KDCO_3 of approximately $10 \times 7 \times 2\text{ mm}$. The 10 Raman lines listed in Table II were observed in the region 2000 to 200 cm^{-1} .

Procedure of Calculation

As noted above, the X-ray analysis of crystalline KHCO_3 ³ definitely indicates that the HCO_3^- ion is dimerized through the $\text{O}-\text{H}\cdots\cdots\text{O}$ bonds to form a ring structure such as shown in Fig. 1. Therefore, the procedure of calculation used for acetic acid dimer¹ can be used with slight modification. Although the molecular model shown in Fig. 1 has C_{2h} symmetry, the spectra obtained in the crystalline state should rather be interpreted on the basis of C_i symmetry, since the site symmetry of the $(\text{HCO}_3)_2^{2-}$ ion is known to be C_i ⁶. Under C_i symmetry, the 9A_g and 3B_g vibrations of the C_{2h} model are grouped into the A_g species, and the 4A_u and 8B_u vibrations are grouped into the A_u species. Nevertheless, we adopted the C_{2h} model in our calculation, because errors due to neglect of the effect of crystal environment on internal vibrations are within the tolerances required for meaningful interpretation of force constants in this paper.

We have calculated only the in-plane vibrations ($9\text{A}_g + 8\text{B}_u$) because most out-of-plane bending vibrations are expected to appear below 200 cm^{-1} except the $\text{O}-\text{H}\cdots\cdots\text{O}$ and CO_3 skeletal bending modes, which can be identified on an empirical basis. The G-matrix elements were evaluated using the molecular parameters obtained from X-ray analysis³: $\text{C}=\text{O}_3$, 1.28 Å; $\text{C}-\text{O}_1$, 1.33 Å; $\text{C}=\text{O}_2$, 1.32 Å; $\text{O}_1-\text{H}\cdots\cdots\text{O}_2$, 2.61 Å; the $\text{O}-\text{H}_1$ distance was estimated to be 1.05 Å by using the relationship, "O-H distance

versus O-H.....O distance" developed by Lippincott and Schroeder.⁹ All the angles were taken as 120° , except ω , which was taken as 180° . The F-matrix elements were expressed by using the modified Urey-Bradley force field described in our previous paper.¹

Table I lists the best set of force constants obtained for the $(\text{HCO}_3)_2^{2-}$ ion. In Table II the calculated frequencies obtained by using this set of force constants are compared with those observed for KHCO_3 and KDCO_3 . The agreement with observed frequencies is quite satisfactory, the maximum deviation being 5.0 % (for ν_1 of KHCO_3), and the average deviation for 32 observed frequencies being 1.9 %. Table II also gives the theoretical band assignments obtained from the calculation of potential-energy distribution in each normal vibration.

1.4 Results and Discussion

Frequencies and Band Assignments

Figure 2 illustrates the infrared spectra of crystalline KHCO_3 and KDCO_3 from 3500 to 160 cm^{-1} . These spectra are similar in general features, but different in fine detail from those published by previous investigators.⁴⁻⁶ For example, Novak et al.⁶ reported four bands at 3070, 2940, 2720, and 2620 cm^{-1} for KHCO_3 , and assigned the former two bands to the combinations between O-H.....O bending and C.....O stretching, and the latter two bands to the O-H stretching modes. We have observed only two distinct bands at 2920 and 2620 cm^{-1} , and have assigned

the former to the same combination band (O-H·····O bend plus C=O stretch), and the latter to the O-H stretching band (ν_{10}). The latter frequency is in good agreement with that predicted from the correlation diagram, "O-H stretching frequency versus O-H·····O distance",¹⁰ which gives a frequency of $\sim 2600 \text{ cm}^{-1}$ for a distance of 2.61 Å. The O-H stretching force constant was adjusted to minimize the errors of ν_1 and ν_{10} of KHCO_3 and KDCO_3 , as seen in Table II. As in the case of the 2920-cm^{-1} band of KHCO_3 , the infrared band at 2240 cm^{-1} of KDCO_3 is assigned to a combination band.

Crystalline KHCO_3 exhibits two strong bands of almost equal intensity at 1650 and 1618 cm^{-1} . Novak et al.⁶ previously assigned the former to the C=O stretching and the latter to the overtone of the out-of-plane bending mode of the CO_3 skeleton at 830 cm^{-1} . However, our calculation gives a better agreement for the Raman-active C=O stretching mode (ν_2) if the band at 1618 cm^{-1} is assigned to the C=O stretching mode (ν_{11}). Although the infrared spectrum of KDCO_3 exhibits three bands (1652 , 1615 , and 1585 cm^{-1}) in this region, the strongest band at 1615 cm^{-1} is assigned to the fundamental for the same reason.

Previously, Novak et al.⁶ assigned the infrared bands at 1405 and 1367 cm^{-1} of KHCO_3 to the coupled vibrations between the O-H·····O in-plane bending and the C=O stretching modes. Calculation of potential energy distribution indicates that the

former (ν_{12}) is an almost pure O-H····O bending mode whereas the latter (ν_{13}) consists of C-O stretching (38 %), C—O stretching (32 %) and O-H····O bending (30 %) modes. Upon deuteration, ν_{12} is shifted to 1050 cm^{-1} whereas ν_{13} is shifted to a slightly higher frequency (1392 cm^{-1}). Because of the shift of O-H····O in-plane bending band to a lower frequency, ν_{13} of KDCO_3 consists of C-O stretching (60 %) and C—O stretching (40%). Corresponding to these infrared active modes, the Raman spectrum of KHCO_3 exhibits two lines at 1448 and 1280 cm^{-1} ; the former is the pure O-H····O bending (ν_3), whereas the latter is a coupled vibration between C—O and C-O stretching modes (ν_4). Upon deuteration, the former is shifted to 1054 cm^{-1} whereas the latter stays at almost the same frequency as before.

The infrared spectrum of KHCO_3 exhibits two bands at 1001 and 988 cm^{-1} . The former is the C-O stretching coupled with the C—O stretching mode (ν_{14}), whereas the latter is the O-H····O out-of-plane bending mode which was not calculated in this paper. The latter assignment is supported by the correlation diagram, "O-H····O out-of-plane bending frequency versus O-H····O distance",¹¹ which predicts a frequency of $\sim 965\text{ cm}^{-1}$ for a distance of 2.61 \AA . Upon deuteration, this band is shifted to $\sim 665\text{ cm}^{-1}$, which is partly hidden by a band at 688 cm^{-1} (ν_{15}). However, ν_{14} of KHCO_3 is shifted only slightly to a lower frequency (985 cm^{-1}) as predicted from the calculation. The Raman-active mode corre-

sponding to ν_{14} is ν_5 which appears strongly near 1025 cm^{-1} in both the compounds. However, the Raman lines corresponding to the O-H-O and O-D-O out-of-plane bending modes were not observed.

The bands at 830 cm^{-1} in the infrared spectra of both the compounds are definitely due to the out-of-plane bending mode of the CO_3 skeleton. This band is always observed between 880 and 800 cm^{-1} in a number of metal carbonates.¹² The corresponding Raman lines appear near 830 cm^{-1} in both the compounds.

The bands at 698 and 655 cm^{-1} in the infrared spectrum of KHCO_3 are assigned to the C=O in-plane bending coupled with the O·····H stretching (ν_{15}) and the O_1CO_2 bending (ν_{16}) modes, respectively. As expected, these frequencies do not change appreciably upon deuteration. The corresponding Raman lines were observed at 676 cm^{-1} (ν_6) and 635 cm^{-1} (ν_7) for KHCO_3 , and at 666 cm^{-1} (ν_6) and 616 cm^{-1} (ν_7) for KDCO_3 . According to the potential-energy distribution, ν_6 is mainly the O_1CO_2 bending mode, and ν_7 the C=O in-plane bending mode in KHCO_3 .

As is seen in Fig. 2, neither of the compounds exhibit any distinct bands between 600 and 300 cm^{-1} . By extending our measurements down to 160 cm^{-1} , we observed only two bands at 248 and 186 cm^{-1} for both the compounds. The potential-energy distribution indicates that the former is the O·····H stretching coupled with the C=O bending mode (ν_{17}). However, the latter does not correspond to any calculated frequency. It may be one of the out-of-

plane ring-deformation modes which were not calculated in this paper. It has been shown previously^{1,2} that the O·····H stretching frequency of the O-H·····O system is little sensitive to deuteration. In the present case, the contribution of the C=O stretching to ν_{17} may further enhance this trend.

The Raman active mode corresponding to ν_{17} is ν_8 , which was predicted at 257 cm^{-1} for both the compounds. However, no Raman lines were observed in this region, probably because they are too weak. It is interesting to note that, different from ν_{17} , this mode is the O·····H stretching coupled with O_1CO_2 bending vibration according to the potential-energy distribution. Finally, the Raman line at 134 cm^{-1} reported for KHCO_3 is in good agreement with the calculated frequency of ν_9 , which is an in-plane ring-deformation mode.

Force Constants

Thus far we have carried out normal-coordinate analyses of acetic acid dimer,¹ the acid carbonate ion, and the acid maleate ion,² all of which have different O-H·····O distances. The O-H and O·····H stretching and the O-H·····O in-plane bending-force constants obtained from these analyses have been plotted against the O-H·····O distance, as is shown in Fig. 3. It is seen that a good linear relationship is obtained for each force constant. Such a diagram will be highly useful in predicting the Urey-Bradley force constants of other hydrogen-bonded systems.

If the straight lines for the O-H and O·····H stretching force constants are extrapolated to an O-H·····O distance of 3.00 Å, the diagram predicts about 7.5 and 0 mdyn/Å, respectively, for these force constants. An example of such an extremely weak hydrogen bond is seen in crystalline LiOH.H₂O, in which the hydroxyl groups form O-H·····OH type hydrogen bonds of 2.99 Å.¹³ The hydroxyl O-H stretching frequency of this compound is reported to be 3547 cm⁻¹.¹⁴ This frequency corresponds to a force constant of ~ 7.10 mdyn/Å, if the OH group in this compound is treated as a diatomic molecule. It seems, therefore, that such a linear relationship between O-H stretching force constant and O-H·····O distance holds over a wide range of O-H·····O distances. This result should be contrasted to the plot of "O-H stretching frequency versus O-H·····O distance",¹⁰ in which the linear relationship breaks down beyond an O-H·····O distance of 2.75 Å.

As is seen in Table I, we have used three different CO stretching force constants in our calculations: $K(C=O_3)$, 7.50; $K(C \text{ --- } O_2)$, 5.50 and $K(C-O_1)$, 4.00 mdyn/Å. On the other hand, the reported X-ray distances are: $C=O_3$, 1.28 Å; $C \text{ --- } O_2$, 1.32 Å and $C-O_1$, 1.33 Å.³ We feel that the latter two values should differ more appreciably than those reported since the O_1 atom is much more strongly bonded to the hydrogen atom than is the O_2 atom. Although we used the values reported by X-ray analysis in this paper, we found that small variations in these values do not

cause any significant changes in our results. It is interesting to note that the average value of these three CO stretching force constants used here is 5.66 mdyn/A, which is close to 5.46 mdyn/A obtained for the CO stretching force constant of the free CO_3^{2-} ion in the Urey-Bradley field.¹⁵ The average value of the three bending force constants around the C atom is 0.44 mdyn/A, which is also close to that obtained for the free CO_3^{2-} ion (0.44 mdyn/A).¹⁵ Although $F(\text{O}_2 \cdots \text{O}_3)$ used here is almost the same as that for the free CO_3^{2-} ion (1.742 mdyn/A),¹⁵ $F(\text{O}_1 \cdots \text{O}_3)$ is smaller than $F(\text{O}_2 \cdots \text{O}_3)$, possibly because the negative charge on the O_1 atom is less than that on the O_2 atom. $F(\text{O}_1 \cdots \text{O}_2)$ is considerably smaller than $F(\text{O}_2 \cdots \text{O}_3)$ because negative charges on the O_1 and O_2 atoms are much less than that on the O_3 atom.

Finally, it is interesting to note that the two stretching-stretching (ρ_1 and ρ_2) and the two bending-bending (l_1 and l_2) interaction force constants used here are 75-80 % larger than those used for acetic acid dimer.¹ This result seems to suggest the presence of stronger vibrational interactions and, consequently, of stronger bonding in potassium acid carbonate than in acetic acid dimer. However, the other two bending-bending interaction constants (l_3 and l_4) used here have the same absolute values (0.08 and 0.04 mdyn/A) as those used for acetic acid dimer, and differ only in sign. A more detailed discussion of the significance of the absolute value and sign of these interaction constants

Will be made after more calculations have been carried out on similar systems.

Table I. Force constants of $(\text{HCO}_3)_2^{2-}$ ion in millidynes per angstrom.

Stretching	Bending	Repulsive
$K(\text{O}-\text{H})=3.20$	$H(\text{O}-\text{C} \cdots \text{O})=0.66$	$F(\text{O}_1 \cdots \text{C} \cdots \text{O}_2)=0.21$
$K(\text{C}-\text{O})=4.00$	$H(\text{O}-\text{C}=\text{O})=0.30$	$F(\text{O}_1 \cdots \text{C} \cdots \text{O}_3)=1.16$
$K(\text{C} \cdots \text{O})=5.50$	$H(\text{O} \cdots \text{C}=\text{O})=0.40$	$F(\text{O}_2 \cdots \text{C} \cdots \text{O}_3)=1.74$
$K(\text{C}=\text{O})=7.50$	$H(\text{C}-\text{O}-\text{H})=0.092$	$F(\text{C} \cdots \text{O}_1 \cdots \text{H}_1)=0.29$
$K(\text{O} \cdots \text{H})=0.76$	$H(\text{C}-\text{O} \cdots \text{H})=0.042$	$F(\text{C} \cdots \text{O}_2 \cdots \text{H}_1')=0.01$
	$H(\text{O}-\text{H} \cdots \text{O})=0.22$	
Stretching-stretching interaction		Bending-bending interaction
$\rho_1=0.175$		$l_1=l_2=-0.11$
$\rho_2=-0.715$		$l_3=-0.08$
		$l_4=0.04$

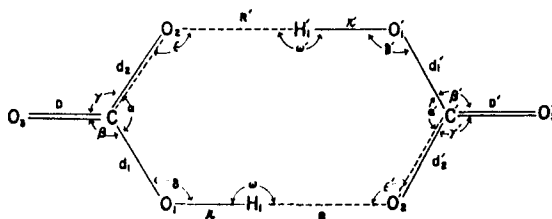


Fig. 1. Molecular model and internal coordinates of $(\text{HCO}_3)_2^{2-}$ ion.

Table II. Comparison of calculated and observed frequencies of $(\text{HCO}_3)_3^{2-}$ and $(\text{DCO}_3)_2^{2-}$ ions in cm^{-1} .

	$(\text{HCO}_3)_3^{2-}$			$(\text{DCO}_3)_2^{2-}$			Band assignment ^b
	Obs. ^a	Calc.	% Error	Obs. ^a	Calc.	% Error	
A_g ν_1	2590 ^c (s)	2702	+5.0	1890 (w)	1952	+3.3	$\nu(\text{O-H})$
ν_2	1682 ^d (m)	1668	-0.8	1668 (m)	1665	-0.2	$\nu(\text{C=O})$
ν_3	1448 ^c (w)	1440	-0.6	1054 (w)	1065	+1.0	$\delta(\text{OHO})$
ν_4	1283 ^d (s)	1289	+0.5	1266 (w)	1289	+3.7	$\nu(\text{C}\cdots\text{O}) + \nu(\text{C=O})$
				1220 (w)			
ν_5	1029 ^d (s)	1044	+1.5	1021 (s)	1032	+1.1	$\nu(\text{C=O}) + \nu(\text{C}\cdots\text{O})$
ν_6	676 ^d (w)	700	+3.6	666 (w)	678	+1.8	$\delta(\text{O}_1\text{CO}_2) + \nu(\text{C-O})$
ν_7	635 ^d (s)	626	-1.4	616 (m)	620	+0.6	$\delta(\text{C=O})$
ν_8	...	258	...	250 (w)	257	+2.8	$\nu(\text{O}\cdots\text{H}) + \delta(\text{O}_1\text{CO}_2)$
ν_9	134 ^d (w)	139	+3.7	...	138	...	ring def.
	$\pi(\text{OHO})$
	832 ^d (w)	825 (m)	$\pi(\text{CO}_2)$
B_u ν_{10}	2620 (w)	2703	+3.2	2055 (w)	1954	-4.9	$\nu(\text{O-H})$
ν_{11}	1618 (s)	1629	+0.7	1615 (s)	1623	+0.5	$\nu(\text{C=O})$
ν_{12}	1405 (s)	1460	+3.9	1050 (s)	1026	-2.3	$\delta(\text{OHO})$
ν_{13}	1367 (s)	1354	-1.0	1392 (s)	1390	-0.1	$\nu(\text{C-O}) + \nu(\text{C}\cdots\text{O}) + \delta(\text{OHO})$
ν_{14}	1001 (m)	973	-2.8	985 (m)	969	-1.6	$\nu(\text{C-O}) + \nu(\text{C}\cdots\text{O})$
ν_{15}	698 (m)	703	+0.7	688 (m)	700	+1.7	$\delta(\text{C=O}) + \nu(\text{O}\cdots\text{H})$
ν_{16}	655 (m)	640	-2.3	630 (m)	636	+0.9	$\delta(\text{O}_1\text{CO}_2)$
ν_{17}	248 (w)	246	-0.8	248 (w)	244	-1.6	$\nu(\text{O}\cdots\text{H}) + \delta(\text{C=O})$
	988 (m)	655 (w)	$\pi(\text{OHO})$
	830 (m)	830 (m)	$\pi(\text{CO}_2)$

^a s, strong; m, medium; w, weak.^b Band assignments are given for the $(\text{HCO}_3)_3^{2-}$ ion; ν , stretching; δ , in-plane bending; π , out-of-plane bending.^c Reference 8.^d Reference 7.

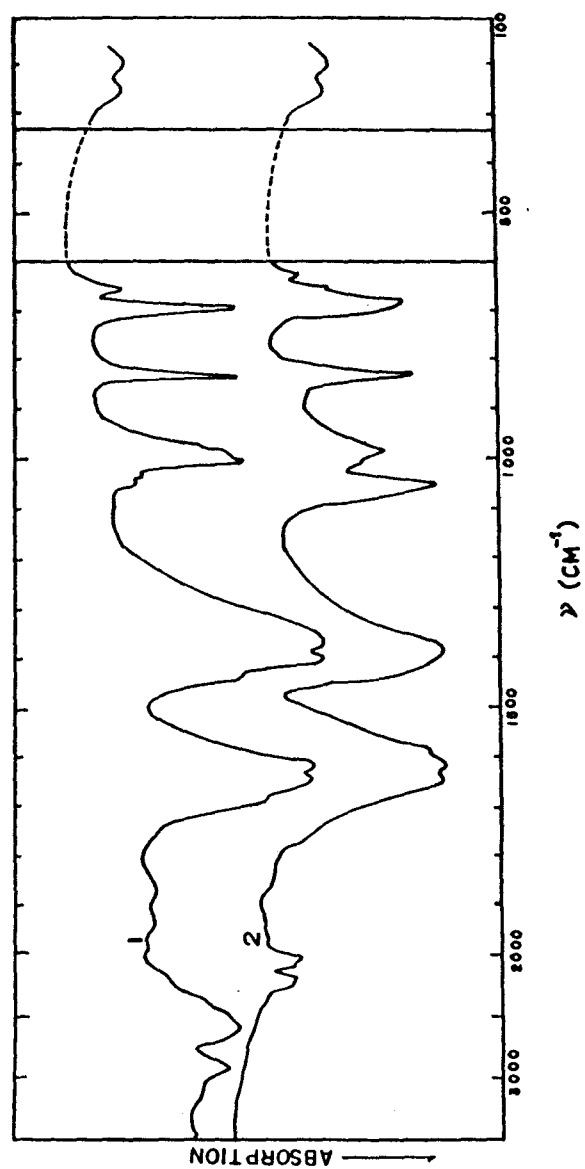


Fig. 2. Infrared spectra of KHCO_3 (1) and KDCO_3 (2).

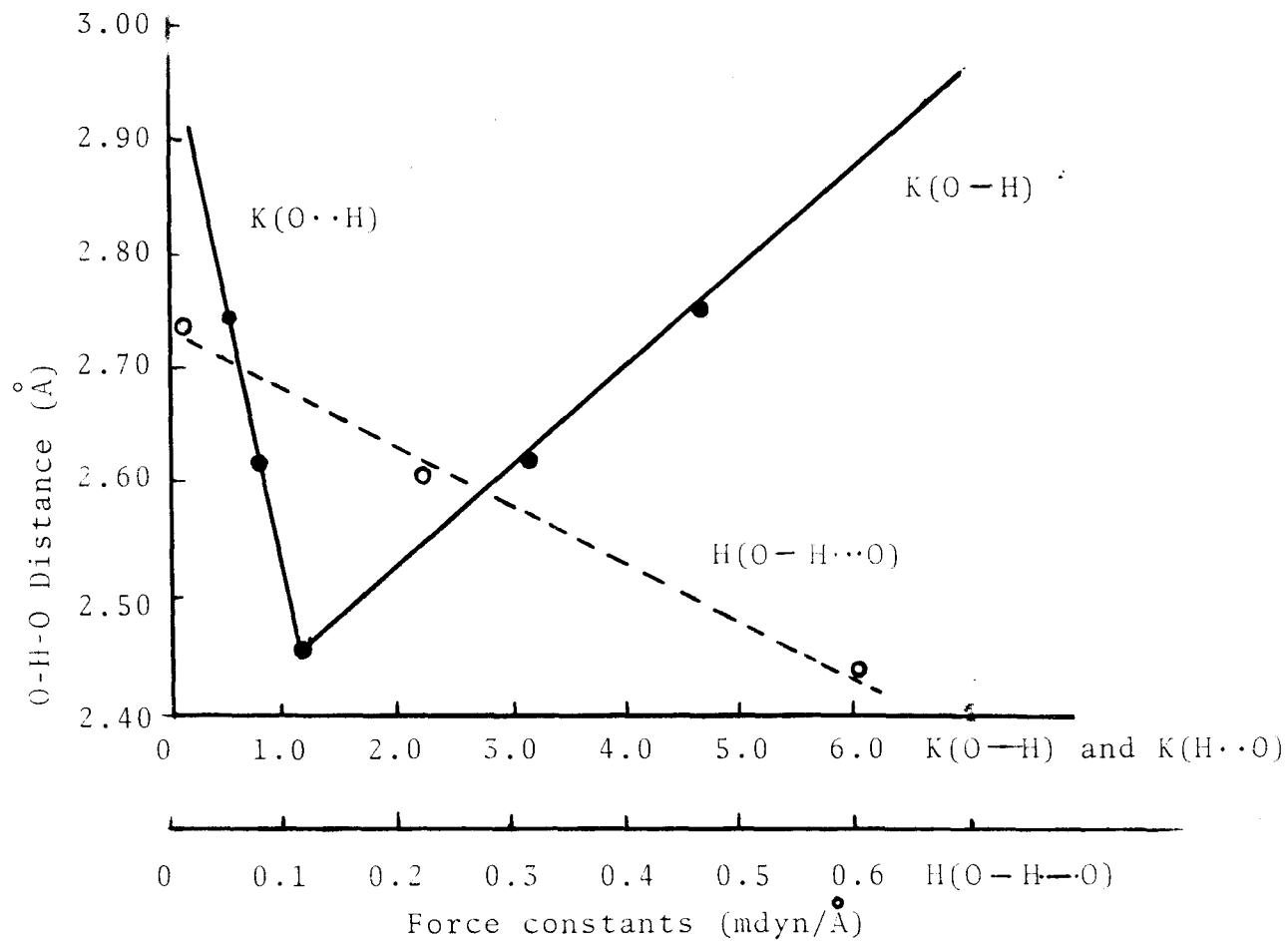


Fig. 3. Plot of O-H...O force constants against O-H...O distance.

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Chapter 2

Normal Coordinate Analysis of Hydrogen Bonded Compounds.
The Enol-Forms of Acetylacetone and Hexafluoroacetylacetone.*¹

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2.1 Summary

The infrared spectra of the enol forms of acetylacetone, hexafluoroacetylacetone, and their deuterio analogs have been measured from 4000 to 70 cm^{-1} . Normal-coordinate analyses have been carried out to estimate the force constants as well as to make theoretical band assignments. The bands at 2750, 1460, 945, and 230 cm^{-1} of nondeuterated acetylacetone have been assigned to the vibrations originating in the $\text{O-H}\cdots\cdots\text{O}$ system. The corresponding force constants are: O-H stretching, 4.00; $\text{O-H}\cdots\cdots\text{O}$ in-plane bending, 0.05; $\text{OH}\cdots\cdots\text{O}$ stretching, 0.30 mdyn/A. Similar calculations have also been carried out for hexafluoroacetylacetone and its deuterio analog. The effect of the substituent on the chelate ring has been discussed by comparing the results obtained for these two molecules.

2.2 Introduction

In previous papers of this series, we have reported the results of normal-coordinate analyses of several hydrogen-bonded compounds containing straight hydrogen bonds.¹ It has also been shown that the O-H stretching force constant decreases and the $\text{O}\cdots\cdots\text{H}$ stretching force constant increases almost linearly as the $\text{O-H}\cdots\cdots\text{O}$ distance decreases.² It is, therefore, of particular interest to calculate the force constants of bent $\text{O-H}\cdots\cdots\text{O}$ bonds, and to compare them with those of straight $\text{O-H}\cdots\cdots\text{O}$ bonds to see

the differences between these two types.

Among a number of compounds containing bent $O-H\cdots O$ bonds, the enol form of acetylacetone serves as an ideal compound for normal-coordinate analysis because of its relatively simple and planar structure. It is well known that acetylacetone exists as a mixture of the enol and keto forms in solution as well as in the gaseous phase. In solution, the percentage of the enol form increases as the polarity of the solvent decreases: 45 % in 10 vol % methylcyanide solution, and 90 % in 10 vol % hexane solution.³ In the gaseous phase, the percentage of the enol form increases as the temperature decreases: ~ 60 % at $230^{\circ}C$ and ~ 95 % at $60^{\circ}C$.⁴ Since the enol form is of interest to us, we have measured the spectra in hexane solution as well as in the gaseous phase at $80^{\circ}C$, where the vapor pressure is sufficient to give clear spectra.

The infrared spectrum of acetylacetone has already been reported by Rasmussen et al.,⁵ Smith,⁶ Bellamy and Beecher,⁷ and Bratoz et al.⁸ in organic solvents, and by Mecke and Funke³ in organic solvents as well as in the gaseous phase. However, most of these measurements were carried out in the NaCl region, and the band assignments were made only on an empirical basis. Furthermore, no spectra have been reported for the deuterio analogs except the d_2 species. We have, therefore, obtained the infrared spectra of the d_0 , d_2 , d_6 , and d_8 species from 4000 to 70 cm^{-1} ,

and have carried out normal-coordinate analysis on all the isotopic species. (The structures of these deutero analogs are shown in Fig. 2.)

In order further to confirm the results obtained for acetylacetone and also to study the effect of the substituent group on the O-H·····O system, we have studied the infrared spectra of hexafluoroacetylacetone and its d₂ analog in the vapor phase. Similar to acetylacetone, this compound also exists as a mixture of the enol and keto forms. Under the same physical conditions, however, the enol form is more predominant in hexafluoroacetylacetone than in acetylacetone.⁹ Since hexafluoroacetylacetone is much more volatile than acetylacetone, the vapor spectrum of the former was easily obtained even at room temperature. It should be mentioned that no complete infrared spectra (4000 to 70 cm⁻¹) of hexafluoroacetylacetone and its d₂ analog have been reported previously. However, the Raman spectrum of the nondeuterated species has been reported by Shigorin and Shevendina.¹⁰

2.3 Experimental

Preparation of Compounds

Acetylacetone, CH₃COCH₂COCH₃, was obtained from Eastman Organic Chemicals and purified by distillation under nitrogen atmosphere. Acetylacetone-d₂ was prepared by refluxing one volume of acetylacetone with five volumes of D₂O, followed by extraction with absolute ethyl ether. This procedure was repeated

several times to ensure complete deuteration. Acetylacetone- d_8 was prepared according to the method of Manyik et al.¹¹ from acetone- d_6 and acetic anhydride- d_6 (both purchased from Merck, Sharp & Dohme, Ltd., of Canada). Acetylacetone- d_6 was prepared by refluxing acetylacetone- d_8 with H_2O for 14 h.

Hexafluoroacetylacetone (purchased from Pierce Chemical Company, Rockford, Illinois) was dried over P_2O_5 overnight, and purified by distillation. Hexafluoroacetylacetone- d_2 was prepared by dissolving hexafluoroacetylacetone in D_2O , followed by dehydration with P_2O_5 .¹²

Spectral Measurements

The infrared spectra in the gaseous phase were measured on a Perkin-Elmer Model 21 infrared spectrophotometer (4000-650 cm^{-1}), a Beckman Model IR 12 infrared spectrophotometer (700-300 cm^{-1}) and a Beckman Model IR 11 far-infrared spectrophotometer (350-70 cm^{-1}). A gas cell equipped with an electrical heater was used to obtain the spectra of acetylacetone and its deuterio analogs in the vapor phase. The temperature was kept at 80°C, where the enol percentage was estimated to be 95 % from the intensity of the 1623- cm^{-1} band. However, the spectra below 350 cm^{-1} were difficult to obtain even under these conditions. We have, therefore, obtained them in 5 % (volume) hexane solution. It has been confirmed that these solutions give spectra almost identical with those of the vapor in the region above 350 cm^{-1} .

It was not necessary to use the heated cell for hexafluoroacetylacetone because the vapor pressure was sufficiently high at room temperature. The window materials used were KBr ($4000\text{--}400\text{ cm}^{-1}$) and polyethylene ($400\text{--}70\text{ cm}^{-1}$).

2.4 Procedure of Calculation

Figure 1 illustrates the molecular model and the internal coordinates used for normal-coordinate analysis. To simplify the calculation, we have assumed that the methyl and trifluoromethyl groups are single atoms having masses of 15.035 and 69.006, respectively. Since the symmetry of this model is C_s , its 21 ($3 \times 9 - 6$) normal vibrations are grouped into 15 A' (in-plane) and 6 A'' (out-of-plane) vibrations. In this paper, we have calculated only the 15 in-plane vibrations using the 21 internal coordinates shown in Fig. 1. As a first step, the G and F matrices were constructed using these 21 internal coordinates. These matrices were reduced to 17th order through a coordinate transformation, which removed four redundancies (concerned with the sum of the angles around each C atom and one concerned with the six angles in the ring). However, the 17th-order A' matrices thus obtained still included two redundancies which were complicated functions of bond distances and angles and which could not be removed easily from the calculation. Therefore, we solved the 17th-order secular equation of the form $|GF - E\lambda| = 0$ using an IBM 7094 computer. The fact that two "zero frequencies" were obtained provided a good

check of our G elements.

Table I lists the symmetry coordinates used for our calculation. The G-matrix elements of acetylacetone were evaluated using the following molecular dimensions: $Z=1.10 \text{ \AA}$, $d_3=d_3'=1.51 \text{ \AA}$, $d_2=1.38 \text{ \AA}$, $d_2'=1.46 \text{ \AA}$, $d_1=1.33 \text{ \AA}$, $d_1'=1.26 \text{ \AA}$, $r=1.18 \text{ \AA}$, $r'=1.34 \text{ \AA}$, $\alpha_1=\alpha_2=\alpha_3=\alpha_1'=\alpha_2'=\alpha_3'=\delta_1=\delta_1'=120^\circ$, $\beta=\beta'=102^\circ$, $\theta=156^\circ$. These values are almost the same as those obtained from X-ray analysis of the enol form of dibenzoylmethane.¹³ The G-matrix elements for hexafluoroacetylacetone were estimated from the same molecular parameters as used above except $d_3=d_3'=1.54 \text{ \AA}$.

The F-matrix elements were expressed by using the simple Urey-Bradley force field.¹⁴ Most force constants were transferred from benzene¹⁵ and acetone,¹⁶ and were adjusted to fit all the isotopic species of acetylacetone or hexafluoroacetylacetone. Table II lists the best set of force constants thus obtained. Table III compares the observed frequencies with those calculated. The agreement is quite satisfactory; the average deviation for 59 observed frequencies of acetylacetone is 1.9 %, and the maximum deviation is 6.6 % for ν_{11} of the d_6 species. For hexafluoroacetylacetone, the average deviation for 30 observed frequencies is 1.5 %, and the maximum deviation is 5.0 % for ν_9 of the d_2 species. In order to make theoretical band assignments, we have calculated the L matrix and the potential-energy distribution¹⁷ for each normal vibration in each symmetry coordinate. The last

column of Table III gives the theoretical band assignments of the nondeuterated species thus obtained. In the same table, the frequencies of all other isotopic species were rearranged so that the frequencies listed in the same row correspond approximately to the vibrational mode of the nondeuterated species listed in the last column. In the following, we discuss mainly the results obtained for the nondeuterated species. However, the results obtained for deuterated species are quoted whenever necessary to substantiate the band assignments for the nondeuterated species.

2.5 Results and Discussion

Acetylacetone

Figures 2 and 3 illustrate the infrared spectra of the enol form of acetylacetone and its three deuterio analogs in the vapor phase and in hexane solution, respectively. A comparison of the d_0 and d_2 spectra is useful in confirming the vibrations due to the O-H.....O and the central (γ) C-H groups while a comparison of the d_0 and d_6 spectra is helpful in locating all the vibrations of the CH_3 groups.

Two weak bands at 3020 and 2960 cm^{-1} of d_0 are definitely due to the C-H stretching modes of the CH_3 groups. The C-H stretching mode (ν_1) of the γ -CH group is weak, and probably hidden under these peaks. In the d_8 compound, all these bands are

shifted to the region around 2200 cm^{-1} . As is seen in Fig.2, it is extremely difficult to define the center of the O-H stretching band (ν_2) because it is broad and weak. However, the d_2 compound exhibits a relatively sharp O-D stretching band at 2020 cm^{-1} . If the same force constant is assumed for both the O-H and O-D bonds, the O-H stretching frequency is estimated to be $\sim 2773\text{ cm}^{-1}$ from the calculations.

The strong and broad bands at $\sim 1615\text{ cm}^{-1}$ of d_0 and d_6 are interpreted as the superposition of the C=O stretching (ν_3) and the C=C stretching coupled with the C-H in-plane bending mode (ν_4). It is interesting to note that this single band is separated into two peaks in the d_2 and d_8 compounds. In accordance with this observation, our calculations provide two different frequencies which are in good agreement with those observed (Table III). This separation is due to the fact that ν_4 is shifted to a lower frequency in the d_2 and d_8 compounds because the contribution of the C-H in-plane bending mode to the C=C stretching mode decreases markedly upon deuteration of the γ -CH hydrogen.

The spectra between 1500 and 1300 cm^{-1} are complicated because the C-O stretching (ν_6), O-H.....O in-plane bending (ν_5), and two CH_3 deformation modes (degenerate and symmetric) are expected to appear in this region. The spectra of the d_2 , d_6 , and d_8 compounds are extremely useful in distinguishing these

modes. In the d_0 compound, the shoulder band at $\sim 1460 \text{ cm}^{-1}$ is assigned to the O-H.....O in-plane bending mode (ν_5) since it is shifted to $\sim 1070 \text{ cm}^{-1}$ in the d_2 and d_8 compounds. The next band at 1432 cm^{-1} of d_0 is interpreted as a superposition of the C-O stretching and the CH_3 degenerate deformation modes, and the band at 1368 cm^{-1} is assigned to the CH_3 symmetric deformation mode. The spectra of the d_6 and d_8 compounds are simple since no CH_3 deformation band appears in this region.

The band at 1250 cm^{-1} of d_0 is assigned to the C-C stretching coupled with the C=C stretching mode (ν_7), and appears strongly in all the compounds studied. The next band at 1170 cm^{-1} is assigned to the C-H in-plane bending (ν_8) overlapped with the CH_3 rocking mode. The fact that the d_6 compound exhibits a relatively strong band at 1180 cm^{-1} supports this assignment. The bands at 945 and 908 cm^{-1} of d_0 are assigned to the OH out-of-plane bending and one of the C- CH_3 stretching modes (ν_9), respectively. It is interesting to note that the latter is shifted to a higher frequency in d_2 and d_8 because it couples with the C-D in-plane bending mode (ν_8 , $\sim 870 \text{ cm}^{-1}$). The strong bands at 764 and 757 cm^{-1} of d_0 and d_6 , respectively, are definitely due to the C-H out-of-plane bending mode, and are shifted to $560\text{--}530 \text{ cm}^{-1}$ in d_2 and d_8 .

A doublet band at 640 cm^{-1} of d_0 is assigned to an out-of-plane ring deformation mode and seems to correspond to a band at

620 cm^{-1} of bis (acetylacetonato) Cu(II).¹⁸ The frequency of this mode decreases gradually as more deuterium is substituted. The same trend is also seen for the bands at 515 cm^{-1} (ν_{11}) and at 364 cm^{-1} (ν_{13}) of d_0 , both of which are assigned to the in-plane ring deformations. A band at 388 (ν_{12}) and a weak shoulder at 320 cm^{-1} (ν_{14}) of d_0 are assigned to the C-CH₃ bending modes, and are shifted very slightly to lower frequencies upon deuteration of the CH₃ hydrogens. The lowest frequency band observed in the hexane solution of d_0 is at 230 cm^{-1} (Fig. 3). According to the potential-energy distribution, this band is due to the O·····H stretching coupled with the OH·····O bending and C-CH₃ bending modes (ν_{15}). Since the hydrogen motion in this mode is very small, it is only slightly sensitive to deuteration.

Hexafluoroacetylacetone

Figure 4 illustrates the infrared spectra of hexafluoroacetylacetone (d_0) and its deuterio analog (d_2) in the vapor phase. The sharp band at 3140 cm^{-1} is clearly due to the C-H stretching mode (ν_1). However, the center of the O-H stretching band is not obvious in the d_0 spectrum. Since the d_2 spectrum exhibits a sharp O-D stretching band at 2240 cm^{-1} , it is possible to estimate the O-H stretching frequency ($\sim 3032 \text{ cm}^{-1}$) assuming the same force constant for both the O-H and O-D bonds.

The sharp strong bands at 1690 and 1636 cm^{-1} of d_0 are assigned to the C=O stretching (ν_3) and the C=C stretching coupled with the C-H in-plane bending mode (ν_4), respectively. As has been discussed previously, they are accidentally overlapped in the case of acetylacetone. This overlapping disappears in hexafluoroacetylacetone because electron-withdrawing inductive effect of the CF_3 group causes a shift of the C=O stretching to a higher frequency (1690 cm^{-1}).

The band at 1448 cm^{-1} is interpreted as a superposition of the C-O stretching (ν_6) and the O-H.....O in-plane bending modes (ν_5), although they are separated into two bands in acetylacetone. Five bands at 1368, 1320, 1270, 1185, and 1090 cm^{-1} of d_0 and those at 1362, 1310, 1232, 1185, and 1040 cm^{-1} of d_2 are assigned to the stretching vibrations of the CF_3 groups. In hexafluoroacetone,¹⁹ they are observed between 1344 and 1200 cm^{-1} . The band at 1225 cm^{-1} of d_0 is assigned to the C-C stretching coupled with the C=C stretching mode (ν_7). The corresponding band of acetylacetone is clearly seen at 1250 cm^{-1} in the absence of the CF_3 group vibrations in this region. The shoulder band at 1108 cm^{-1} of d_0 is assigned to the C-H in-plane bending mode (ν_8), and is shifted to 880 cm^{-1} in d_2 .

The band at 913 cm^{-1} is assigned to the O-H.....O out-of-plane bending mode and is shifted to 634 cm^{-1} upon deuteration. The bands at 855 (shoulder), 740, and 816 cm^{-1} of d_0 are assigned to

the C-CF₃ stretching modes (ν_9 and ν_{10}) and one of the CF₃ group deformation modes.²⁰ All these vibrations are only slightly shifted upon deuteration. The strong band at 647 cm⁻¹ of d₀ is assigned to an out-of-plane ring deformation mode which corresponds to the band at 640 cm⁻¹ in acetylacetone. In d₂, this band is assumed to be overlapped by the O-D·····O out-of-plane bending mode.

The strong band at 573 cm⁻¹ is assigned to another deformation mode of the CF₃ group.²⁰ Two medium intensity bands at 522 and 324 cm⁻¹ of d₀ are attributed to the in-plane ring deformation modes, ν_{11} and ν_{13} , respectively. Also two weak bands at 438 and 145 cm⁻¹ are assigned to the C-CF₃ in-plane bending modes, ν_{12} and ν_{14} , respectively. The bands at 255 and 240 cm⁻¹ are tentatively assigned to the CF₃ rocking modes¹⁹ which are not calculated in this paper. As is seen in Fig. 4, the strong band at 240 cm⁻¹ has a shoulder at ~ 228 cm⁻¹, which correspond to the band at 230 cm⁻¹ (ν_{15}) of acetylacetone. Two bands at 106 and 90 cm⁻¹ of d₀ may be due to the torsional modes of the CF₃ groups. This mode is reported to appear at 84 cm⁻¹ in CF₃CF=CF₂.²¹

Force Constants

Table II lists the best sets of force constants obtained for the enol forms of acetylacetone and hexafluoroacetylacetone. Among these force constants, the stretching force constants are most sensitive to the changes in bond strength. Therefore, the values of these

values of these force constants for the two molecules are compared in Fig. 5. It is possible to explain the differences in these force constants on the basis of the differences in electronic effect between the CF_3 and CH_3 groups. As a first approximation, we assume that the inductive effect of these groups is more important than the mesomeric effect. To discuss the inductive effect of the substituent group on the chelate ring, we may consider the effects of two CF_3 or CH_3 groups separately. In hexafluoroacetylacetone, the strong electron-withdrawing property of the CF_3 group (see Fig. 5) will increase the double-bond character of the $\text{C}=\text{O}_2$ bond, resulting in a considerable decrease in the charge density of the lone-pair electron on the O_2 atom. On the other hand, it will weaken the C-C bond as has already been demonstrated by the normal-coordinate analyses of C_2H_6 and C_2F_6 .¹⁴ Since the CH_3 group is rather slightly electron donating, its effects on the chelate ring may occur in the opposite direction to those described above. Therefore, the C=O stretching force constant is larger and the C-C stretching force constant is smaller in hexafluoroacetylacetone than in acetylacetone.

The effect of the second substituent group can be explained similarly. Relative to the CH_3 group, the CF_3 group will strengthen both the C=C and $\text{C}-\text{O}_1$ bonds. Thus their force constants are larger in hexafluoroacetylacetone than in acetyl-

acetone. According to our calculations, however, the O-H and O·····H stretching force constants of the former are larger and smaller, respectively, than those of the latter. This result can only be interpreted if we assume that the strength of the O₂·····H bond in these compounds is mainly determined by the basicity of the O₂ atom (charge density of the lone-pair electron).²² Since the O₂ atom of acetylacetone is more basic than that of hexafluoroacetylacetone, the former forms a stronger O·····H bond and a weaker O-H bond than the latter.

Burdett and Rogers⁹ plotted the C=O stretching frequencies of hexafluoroacetylacetone, trifluoroacetylacetone, acetylacetone, and dibenzoylmethane against the chemical shifts of the OH protons, and noted considerable deviations from a linear relationship for the former two compounds. However, they assigned the bands at 1633 and 1600 cm⁻¹ of hexa- and trifluoroacetylacetones, respectively, to the C=O stretching modes. Figure 6 shows that a good linear relationship exists if the higher frequency bands at 1690 and 1655 cm⁻¹ of these compounds are assigned to the C=O stretching modes. It is concluded, therefore, that the lower the C=O₂ stretching frequency, the stronger the O₂·····H bond and the lower the magnetic field of the proton resonance, since the H atom is less shielded. Thus, the results shown in Fig. 6 are interpreted to indicate that the strength of the O-H·····O bond will decrease in the order: dibenzoylmethane > acetylac-

tone > trifluoroacetylacetone > hexafluoroacetylacetone.

Recently, Kondo et al.²³ have noted that the magnetic field of the proton resonance becomes higher as the acidity of the enol form increases in the above order of β -diketones. This result again seems to support our interpretation that the basicity of the O_2 atom rather than the acidity of the O-H bond determines the magnitude of the electron shielding around the H atom.

We have previously shown² that the O-H stretching force constant decreases and the $O\cdots H$ stretching force constant increases almost linearly as the $O\cdots O$ distance of the straight hydrogen bond decreases. These relationships predict ~ 2.0 and 1.0 mdyne/\AA for a distance of 2.5 \AA which is found in acetylacetone and hexafluoroacetylacetone. It is evident, therefore, that they are not applicable to bent hydrogen bonds. As has been pointed out by Schneider,²⁴ the hydrogen bond is the strongest when the O-H bond is collinear with the direction of the lone-pair orbital of the O_2 atom. This condition is satisfied in the three hydrogen-bonded compounds studied thus far, acetic acid dimer, the acid carbonate ion, and the acid maleate ion, all of which contain linear hydrogen bonds of various $O-H\cdots O$ length.² It is evident that this condition cannot be met in intramolecular hydrogen-bonded compounds such as acetylacetone and hexafluoroacetylacetone. Aside from the collinearity of the $O-H\cdots O$ bond, the direction of the lone-pair orbital of the O_2 atom (120°

from the $C=O_2$ bond) deviates by 18° from that of the $O\cdots\cdots H$ bond obtained from X-ray analysis ($C-O_2-H$ angle, 102°).¹³ Therefore, it is not surprising to find large deviations of the $O-H$ and $O\cdots\cdots H$ stretching force constants of the bent hydrogen bonds from the linear relationships obtained for straight hydrogen bonds.

Table I. Symmetry coordinates for in-plane vibrations.

Symmetry coordinate	Vibration mode
$S_1 = \Delta Z$	$\nu(C-H)$
$S_2 = \Delta r$	$\nu(O-H)$
$S_3 = \Delta d_1'$	$\nu(C=O)$
$S_4 = \Delta d_2$	$\nu(C=C)$
$S_5 = (1/6^{1/2})(2\Delta\Theta - \Delta\beta - \Delta\beta')$	$\delta(O-H)$
$S_6 = \Delta d_1$	$\nu(C-O)$
$S_7 = \Delta d_2'$	$\nu(C-C)$
$S_8^a = \Delta\delta_1 - \Delta\delta_1'$	$\delta(C-H)$
$S_9 = \Delta d_3'$	$\nu(C-R')$
$S_{10} = \Delta d_3$	$\nu(C-R)$
$S_{11} = (1/6^{1/2})(2\Delta\delta - \Delta\alpha_1 - \Delta\alpha_1')$	Ring def
$S_{12}^a = \Delta\alpha_2 - \Delta\alpha_3$	$\delta(C-R)$
$S_{13} = (1/\sqrt{2})(\Delta\beta - \Delta\beta')$	Ring def
$S_{14}^a = \Delta\alpha_2' - \Delta\alpha_3'$	$\delta(C-R')$
$S_{15} = \Delta r_1'$	$\nu(O\cdots H)$
$S_{16} = (1/6^{1/2})(\Delta\alpha_1 + \Delta\alpha_1' + \Delta\delta - \Delta\beta - \Delta\beta' - \Delta\Theta)$	Ring def
$S_{17} = (1/\sqrt{2})(\Delta\alpha_1 - \Delta\alpha_1')$	Ring def

^a These coordinates are not normalized.

ν , stretching; δ , bending.

Table II. Urey-Bradley force constants of acetylacetone and hexafluoroacetylacetone
(in millidynes per angstrom).

	Stretching			Bending			Repulsive	
	R,R'=CH ₃	R,R'=CF ₃		R,R'=CH ₃	R,R'=CF ₃		R,R'=CH ₃	R,R'=CF ₃
<i>K</i> (C-O)	5.800	6.100	<i>H</i> (O ₁ -C=C)	0.185	0.500	<i>F</i> (O ₁ ...C...C)	0.400	0.400
<i>K</i> (O=O)	8.820	9.700	<i>H</i> (R-C=C)	0.235	0.200	<i>F</i> (R...C...C)	0.300	0.300
<i>K</i> (C=C)	5.650	6.200	<i>H</i> (R-C-O ₁)	0.100	0.320	<i>F</i> (R...C...O ₁)	0.200	0.800
<i>K</i> (C-C)	4.800	4.300	<i>H</i> (O ₂ =C-C)	0.200	0.500	<i>F</i> (O ₂ ...C...C)	0.350	0.350
<i>K</i> (C-R)	4.100	4.300	<i>H</i> (R'-C-C)	0.225	0.180	<i>F</i> (R'...C...C)	0.300	0.210
<i>K</i> (C-R')	4.000	4.200	<i>H</i> (R'-C=O ₂)	0.160	0.390	<i>F</i> (R'...C...O ₂)	0.100	1.000
<i>K</i> (O-H)	4.000	4.800	<i>H</i> (C=C-C)	0.300	0.300	<i>F</i> (C...C...C)	0.370	0.370
<i>K</i> (O...H)	0.300	0.128	<i>H</i> (C=C-H)	0.280	0.250	<i>F</i> (C...C...H)	0.150	0.160
<i>K</i> (C-H)	4.650	5.100	<i>H</i> (C-C-H)	0.300	0.220	<i>F</i> (C...C...H)	0.150	0.160
			<i>H</i> (C-O ₁ -H)	0.515	0.490	<i>F</i> (C...O ₁ ...H)	0.400	0.450
			<i>H</i> (H...O ₂ =C)	0.100	0.070	<i>F</i> (H...O ₂ ...C)	0.010	0.010
			<i>H</i> (O ₁ -H...O ₂)	0.050	0.050	<i>F</i> (O ₁ ...H...O ₂)	0.001	0.002

	R, R' = CH ₃								R, R' = CF ₃				Band assignment ^b
	d ₁		d ₂		d ₃		d ₄		d ₅		d ₆		
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	
ν_1	2960	2961	2200	2202	3060	2961	2237	2202	3140	3116	2320	2303	ν (C-H)
ν_2	2750	2773	2020	2043	2650	2773	1960	2043	2965	3032	2240	2202	ν (O-H)
ν_3	(1623)	1622	1630	1618	(1610)	1620	1627	1617	1690	1686	1677	1680	ν (C=O)
ν_4	(1623)	1600	1545	1544	(1610)	1600	1535	1543	1636	1625	1585	1595	ν (C=C) + δ (CH)
ν_5	1460*	1457	1076	1055	1467*	1461	1071	1055	(1448)	1439	(1040)	1040	δ (O-H...O)
ν_6	(1432)	1411	1380	1389	1447	1411	1380	1382	(1448)	1413	1413	1412	ν (C-O)
ν_7	1250	1216	1270	1273	1265	1214	1258	1270	1225	1215	1232	1278	ν (C-C) + ν (C=C)
ν_8	(1170)	1173	869	851	1180	1178	875*	840	1108*	1104	880	882	δ (C-H)
ν_9	908	878	928	956	900	861	902	945	855*	878	855	812	ν (C-R)
ν_{10}	810	845	...	785	795	832	788	771	740	799	735	704	ν (C-R)
ν_{11}	515	527	500	521	470	502	470	496	522	516	508	512	Ring def
ν_{12}	388	379	386	372	360	367	360	361	438	456	430	443	δ (C-R)
ν_{13}	364	363	360	357	337	354	386	349	324	326	314	319	Ring def
ν_{14}	320*	319	314*	315	310	312	290*	308	145	143	143	142	δ (C-R)
ν_{15}	230	223	227	221	212	211	208	209	228	227	226	225	ν (O...H) + δ (O-H...O) + δ (C-R)
	3020		3020						1368		1362		ν (R)
									1320		1310		
									1270		1232		
									1185		1185		
									1090		(1040)		
	(1432)		1422		1062		1107		816		791		$\delta_{\text{as}}(\text{R})$
	1368		1365		1038		1042		573		567		$\delta_{\text{a}}(\text{R})$
	945		702		945		684		913		(634)		ν (O-H)
	(1170)		1178		795		810		240		240		
	995		1022		(757)		765		255*		253*		$\nu_{\text{as}}(\text{R})$
	764		560		(757)		531		713		(508)		ν (C-H)
	(640)		632		610		594		647		(634)		Ring def (ν)
			612		594		585*						
									106		112		Torsion (R)
									90		87		

* Asterisks indicate shoulder, and parentheses indicate overlap.

^b Band assignments are given for the δ compounds. δ_{a} , δ_{as} , ν_{as} , and ν denote degenerate deformation, asymmetric deformation, rocking, and out-of-plane bending modes, respectively.

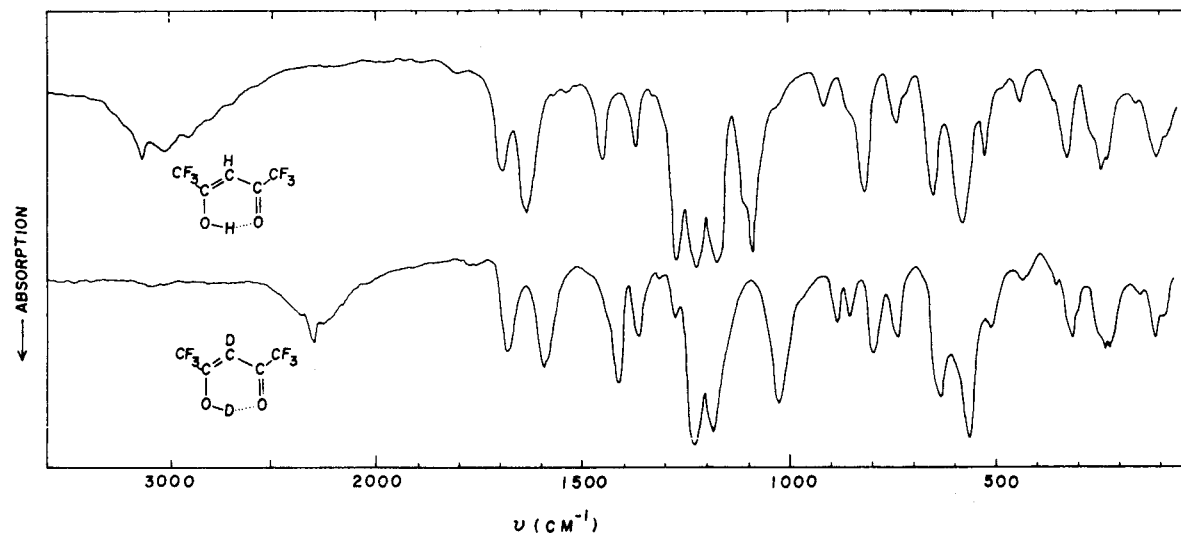


Fig. 4. Infrared spectra of enol forms of hexafluoroacetylacetone and its deuterio analog in the vapor phase.

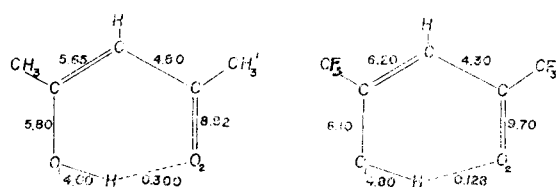


Fig. 5. Comparison of stretching force constants of acetylacetone and hexafluoroacetylacetone (millidynes per angstrom).

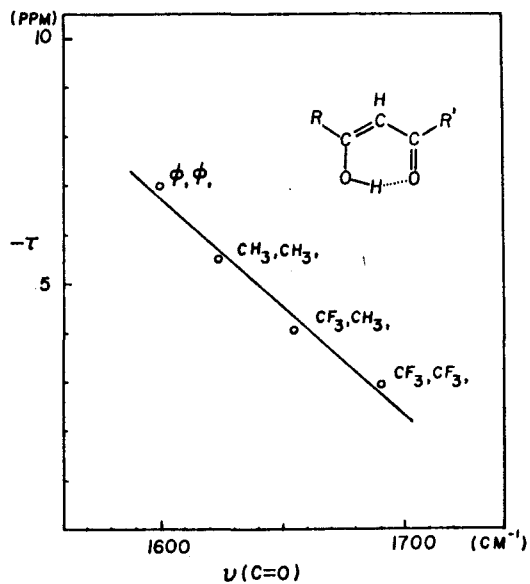
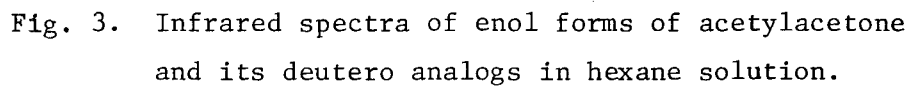
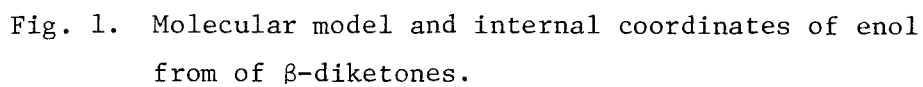


Fig. 6. Plot of proton chemical shift against C=O stretching frequency.



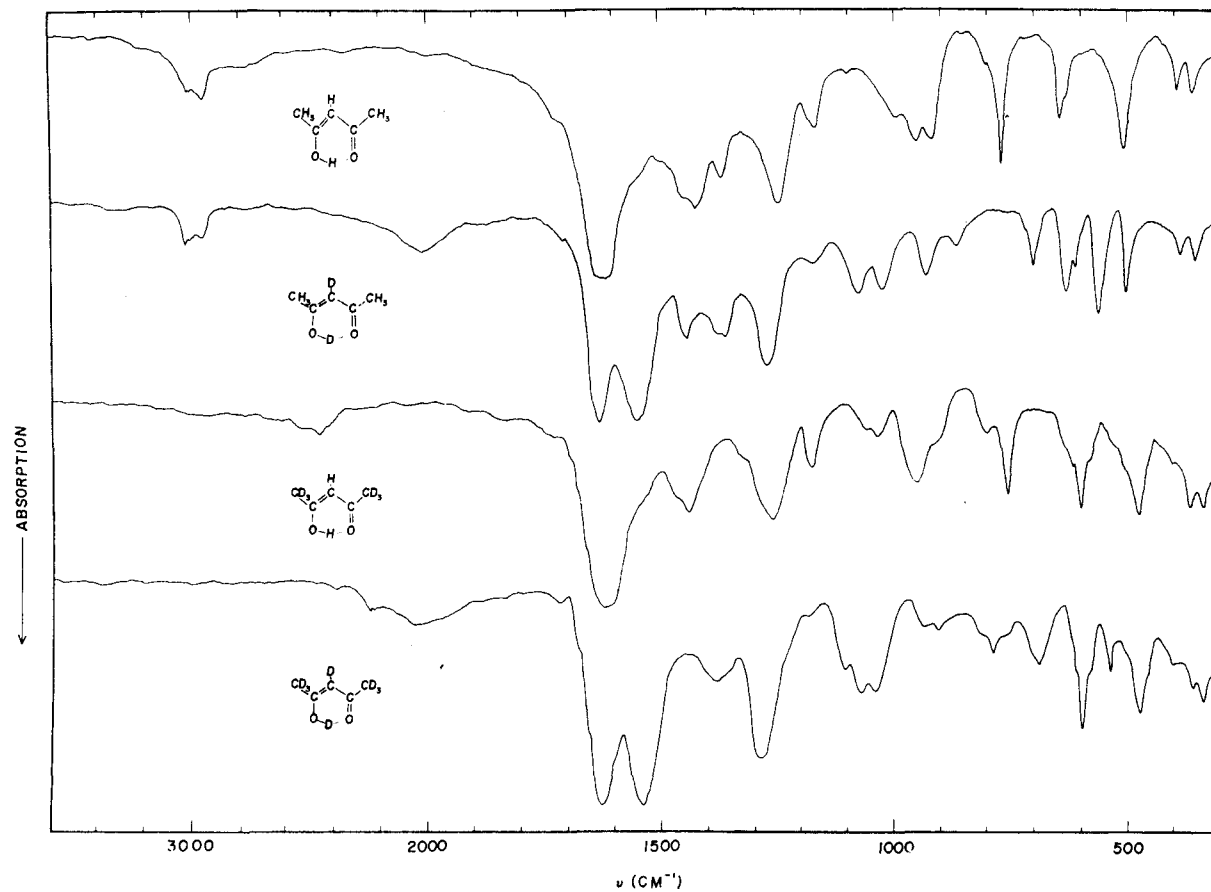


Fig. 2. Infrared spectra of enol forms of acetylacetone and its deuterio analogs in the vapor phase.

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Chapter 3

Intramolecular Hydrogen Bond in Enol-Form of 3-Substituted-2,4-pentanedione.*¹

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*1 Presented in part at the 20th Annual Meeting of the Chemical Society of Japan at Tokyo, April 1967. and the General Discussion on Molecular Structure held at Sapporo, Oct. 1967.

3.1 Summary

Spectroscopic characteristics of highly enolized tautomers of 3-substituted-2,4-pentanediones have been studied with infrared and nuclear magnetic resonance methods. The linear relationship between the chemical shifts of enolic proton and the chelated carbonyl stretching vibrations has been established for the various 3-substituted-2,4-pentanediones. The stronger electron-withdrawing resonance effect of the substituent at 3-position results in the lower magnetic field shift of the enolic proton and the lower frequency shift of the chelated carbonyl stretching. The synthesis and structure in tautomeric equilibrium of new 3-substituted-2,4-pentanediones are described.

3.2 Introduction

Forsen and Nilsson¹⁻⁴ have extensively investigated enolized β -triketones using nmr and infrared spectroscopies and found the good linear relationship between the chemical shifts of enolic proton and the carbonyl stretching vibration. On the other hand, Burdett and Rogers⁵ have found that this correlation is not kept for the system of β -diketones. However, the correct band assignments to carbonyl stretching according to the normal coordinate analysis give the similar linear relationship for the β -diketone system as pointed out by Ogoshi and Nakamoto.⁶ Of the spectra of β -diketones, the nmr spectra have been already reported for

acetylacetone,^{5,7} 3-methyl-^{5,7}3-chloro-,⁷3-formyl-⁴ (in chloroform and dimethylsulfoxide), and 3-acetyl-2,4-pentanedione.⁸ Infrared spectroscopic study on 3-cyano-2,4-pentanedione by Wierzchowsky and Shugar⁹ has shown that it completely enolizes both in the crystalline state and carbon tetrachloride solution. For 3-chloro-2,4-pentanedione and 2,4-pentanedione, Mecke and Funke¹⁰ have reported the infrared spectra from 4000 to 400 cm^{-1} with the empirical band assignment. In order further to confirm the results obtained for the above mentioned diketones and to study systematically the effect of the substituents on the intramolecular hydrogen bonding, we have investigated the nmr and infrared spectra of 3-substituted-2,4-pentanediones including those of which spectra have never been reported. The structural from of new compounds in tautomeric equilibrium will be discussed in this paper.

3.3 Experimental

Preparation of Compounds

3-Nitro-2,4-pentanedione (VII). Bis-(3-nitro-2,4-pentanediono)-Cu(II) was prepared according to the method of Collman et al.¹¹ The finely pulverized powder of the complex (15.0g) suspended in 150 ml. of chloroform was shaken with 150 g. of EDTA diammonium dissolved in 150 ml. of water, until the green color of the chloroform layer disappeared. The chloroform solution was

washed with a small amount of water and dried over anhydrous sodium sulfate. After removing chloroform, distillation gave 12.2 g. (87.7 %) of diketone as a pale yellow liquid; bp 72.5-73.0° (8 mm.).

Anal. Calcd. for $C_5H_7O_4N$: C, 41.39 %; H, 4.86 %; N, 9.65 %.

Found C, 41.39 %; H, 4.99 %; N, 9.75 %.

3-Carbomethoxy-2,4-pentanedione (XI). (methyl diacetylacetate).

The procedure was slight modification of the method reported by Spassow,¹² using methyl acetoacetate in stead of ethyl acetoacetate. The product was purified by precipitation as violet copper (II) chelate with aqueous copper (II) acetate and subsequent contact of the chloroform solution of the complex with the aqueous EDTA diammonium. The colorless liquid was distilled at 94.0-94.5° (24 mm). The total yield was 21 % based on methylacetoacetate.

Anal. Cal. for $C_7H_{10}O_4$: C, 53.17 %; H, 6.23 %; Found C, 53.38 %; H, 6.31 %.

3-Methylthio-2,4-pentanedione (IX). A solution of methylmercaptane (7.5 g.) in methanol (20 ml.) was dropwisely added to the stirred mixture of 3-chloro-2,4-pentandione (II) (19.0 g.) and pyridine (12.0 g.) at 0°. The reaction mixture was further stirred for 2 hr at room temperature. After methanol was removed under vacuum, pyridine hydrochloride crystalized from the solution was filtered off. Carbon tetrachloride (100 ml.) was added to

the filtrates.

The carbon tetrachloride solution was separated from solid material, washed with water, and dried over sodium sulfate overnight. The distillation gave the pale yellow liquid (4.6 g.), bp 75.0-75.7° (16 mm). The copper (II) chelate was gradually decomposed upon standing.

Anal. Cald. for $C_{10}H_{10}O_2S$: C, 49.31 %, H, 6.85 %; S, 21.92 %.

Found C, 49.45 %; H, 6.80 %; S, 22.21 %.

The remaining materials were prepared according to the well established methods listed in Table I. Acetylacetone was commercially available and purified by distillation under nitrogen atmosphere.

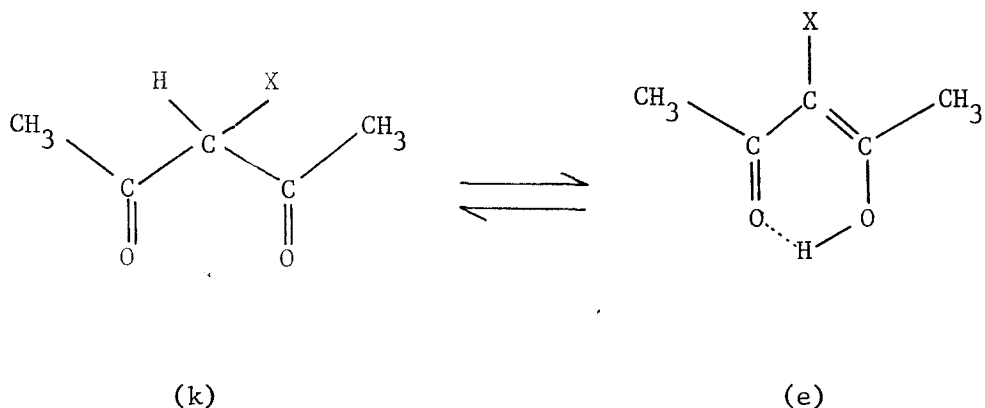
Spectral measurements

Proton magnetic resonance spectra in carbon tetrachloride solution were recorded on a Jeolco JNM SH-60 spectrometer. Concentration was changed from ca. 20 % to ca. 1 % at 25°C. Values of chemical shift are reported in τ (ppm) from internal tetramethylsilane. A Jasco DS-402G spectrophotometer was used to obtain the infrared spectra ($4000-800\text{ cm}^{-1}$) in carbon tetrachloride at 25°C.

3.4 Result and Discussion

It has been known that β -diketone exists as a mixture of the enol (e) and the keto form (k), of which ratio in tautomeric equilibrium is influenced by some factors such as temperature

and solvents.



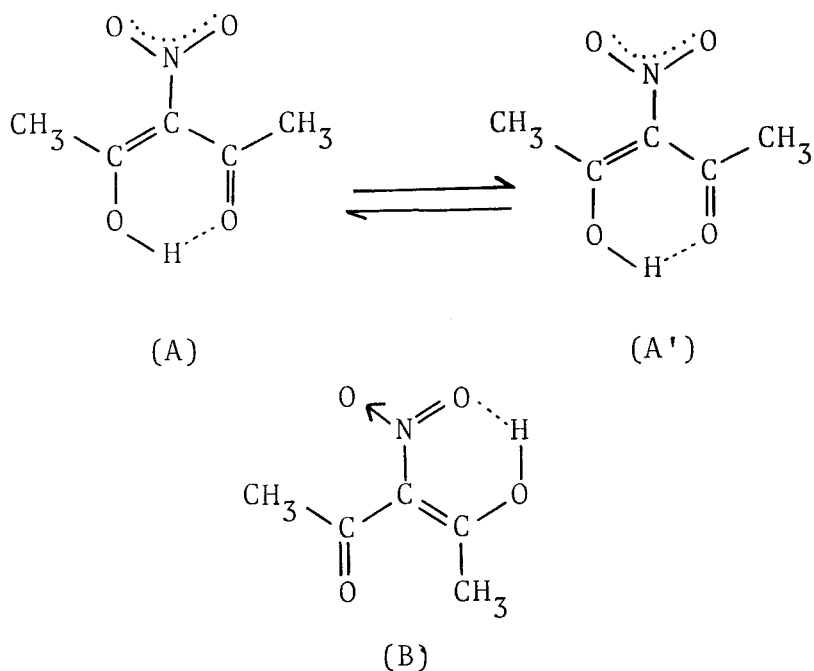
X=H (I), Cl(II),¹³ -CH=CH-CH₃ (III),¹⁴ -CH=CH-C₂H₅ (IV),¹⁵
 -CH₂-CH=CH₂ (V),¹⁶ -CN(VI),¹⁶ -NO₂ (VII), -SCN(VIII),¹⁷ -SCH₃ (IX),
 -COCH₃ (X),¹⁸ -COOCH₃ (XI), -COOC₂H₅ (XII),¹² -CHO (XIII)⁴

Table 1 lists frequencies of carbonyl stretching, chemical shifts, and the percentages of enol form in carbon tetrachloride. Collman et al.¹¹ have reported that hydrolysis of bis-(3-nitro-2,4-pentanedieno)-Cu(II) with acid yields intractable oily material. We followed the same procedure as they tried and separated the white crystal confirming as **nitroacetone**; mp 46.3° (lit.²⁰ mp 46.5°). The alternative method, that is, the exchange of metal ion with proton using the aqueous EDTA diammonium proved to be useful method to isolate free ligand without decomposition.

Figure 1 shows the infrared spectra of VII in the carbon tetrachloride solution. A medium shoulder band at around 1600 cm⁻¹ is assigned to the overlapping band of the C=O stretching and the C=C stretching. The two strong absorptions at

at 1526 and 1351 cm^{-1} are assigned to the asymmetric and the symmetric stretching of nitro group, respectively. Another strong and sharp band at 825 cm^{-1} seems to be the C-NO_2 stretching mode. As is seen in Table I, the nmr spectrum of VII in carbon tetrachloride shows the presence of an enolic proton at -6.95 ppm and two methyl groups attached to the chelate ring as a singlet at 7.54 ppm.

In the enol form of VII, one may suppose the different forms as shown below.

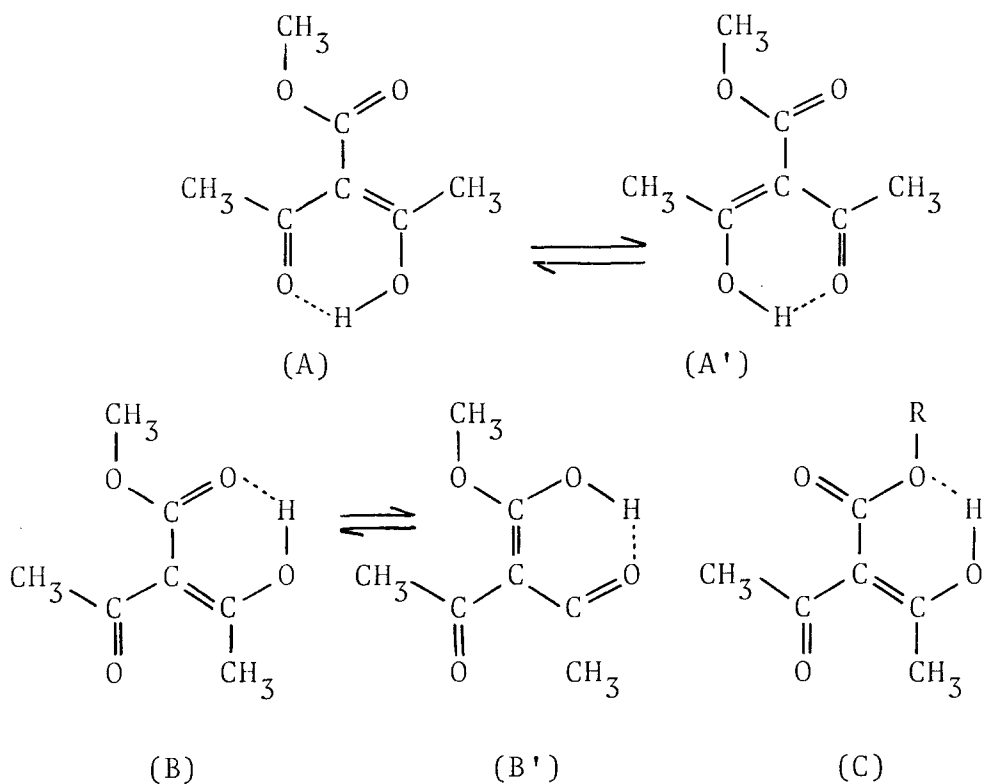


The chelate ring of (A) or (A') is the same as that of acetylacetone, whereas the oxygen of nitro group can act as a proton acceptor to form another type of the chelate ring (B). As

a matter of fact, ir and nmr data suggest that the tautomeric equilibrium is remarkably shifted to increase the enol tautomer by the substitution with the nitro group, and the presence of singlet methyl proton might be an evidence that the enolic form (A) or (A') is more stable than (B). Kluiber²¹ reported that VIII prepared by the reaction of copper chelate of acetylacetone with thiocyanogen in the absence of sodium bicarbonate has infrared absorptions at 2208, 1739, and 1588 cm^{-1} . The observed absorption at 1739 cm^{-1} suggested the existence of the keto form to some extent. However, our careful investigation indicates that VIII is entirely enolized in the carbon tetrachloride solution and also crystalline state based on nmr and infrared spectra (Table 1 and Figure 1). The nmr spectrum of VIII shows the two singlet peaks at 7.50 and -7.10 ppm which are assigned to six protons of methyl and one proton of enol. Moreover, the carbonyl stretching of the keto form appeared at around 1700 cm^{-1} has never been observed in the infrared spectrum.

The X-ray crystallographic studies^{22,23} have suggested that the planar chelate ring is proved to be essentially asymmetric structure about the position of proton between two oxygens. If that is true, there must be observed two different kinds of chemical shifts of the methyl groups jointed to the chelate ring. It has, however, been known that the chemical shifts of two methyl groups are usually observed as the averaged singlet

peak²⁴ except for the metal complexes of some acetylacetonate.²⁵ As has been pointed out by Forsen,⁴ many different enolic forms are possible in some β -triketones. Thus we can represent three types of enol forms as shown below. The interconversion between A and A' as well as B and B' can occur by a movement of enolic



hydrogen along the hydrogen bond. Since the alkoxy oxygen acts as a weaker base, the enolic form C seems to be less favorable compared with A (or A') and B (or B'). The mmr spectrum of XI shows three singlet peaks at 7.65 ppm (6H), 6.25 ppm (3H) and -7.97 ppm (1H) assigned to the two methyl groups attached to

chelate ring, the methyl of methoxy and enolic proton respectively as is seen in Figure 2. It is convinced that the enol form A (or A') is the most stable among them, otherwise the chemical shifts of different methyl groups must exhibit at least more than three peaks in this region. The nmr spectrum of XII in Figure 3 can be similarly explained to support the exclusive existence of the enol form corresponding to A or (A'). On the other hand, the three chelate species are distinguished for 3-formyl-2,4-pentanedione XIII from the nmr spectra in chloroform-dimethylsulfoxide solution. Thus it is shown that the enol form corresponding to the form A (or A') amounts to about 80 %, whereas the rest of about 20 % are the two internal isomers B and B'.⁴

M. E. McEwntee et al.¹⁴ and G. B. Payne¹⁵ have suggested that 3-propenyl-(III) and 3-butenyl-2,4-pentanedione (IV) are highly enolized. However, no available spectra of nmr has never been reported so far. In the infrared spectrum of III the C=C stretching has not been detected, since the conjugation of C=C of the alkenyl group with the chelate ring decreases the frequencies of C=C and causes a eventual overlapping with the strong C=O stretching at 1607 cm^{-1} . The strong absorption at 970 cm^{-1} is assigned to the wagging mode of trans C-H of olefinic group. This suggests that III exists only in the trans form about the propenyl group (Figure 4). As shown in Figure 4, the nmr spec-

trum indicates that III are highly enolized (ca. 93 %) in carbon tetrachloride. On the contrary, the substitution of allyl group at the 3-position increases the percentage of the keto tautomer (49 %) in the comparable order to that (61 %) of 3-n-propyl derivative.²⁶ It should be noted that the π - π conjugation of a substituent double bond with the chelate ring significantly enhances the stability of the chelate ring, but seems to give small effect on the strength of hydrogen bonding, since the chemical shift of enol proton is not so much different from that of 3-allyl derivative (V). The chemical shift of enol proton of V appears at -6.60 ppm. as a singlet in carbon tetrachloride.

Figure 5 illustrates infrared spectra of III and V from 1800 to 1500 cm^{-1} . The strong absorption at 1731 and 1705 cm^{-1} in V are assigned to the carbonyl stretching vibrations of the keto form, whereas the strength of those bands at around 1700 cm^{-1} extremely decreases in III. The hydrogen-bonded carbonyl stretching of III and V give the strong absorptions at 1607 and 1606 cm^{-1} , respectively. Moreover, the sharp band at 1640 cm^{-1} of V is possibly assigned to the C=C stretching of allyl group. The comparison of the both spectra seems to support our above interpretation again. The sulfur atom has an electron donating resonance ability using its 3p orbital (non-bonding electron) as well as an electron accepting resonance ability using its 3d orbital (or the hybrid orbital including 3d orbital). It is,

therefore, of particular interest to investigate the effect of substituents containing sulfur atom on chelate ring and its tautomeric equilibrium.

However, no preparative method has been reported as concerns carbon-sulfur bond formation at 3-position of 2,4-pentanedione except 3-thiocyano-¹⁸ and 3-(o-nitrophenylthio)-derivatives.²⁷ We have succeeded in the first nucleophilic substitution of 3-chloro-2,4-pentanedione (γ -chloroacetylacetone) by the reaction with methylmercaptane in the presence of pyridine. The nmr and ir spectra of the obtained 3-methylthio-2,4-pentanedione (IX) are shown in Figures 6 and 7, respectively. The high enol percentage of IX is confirmed by both nmr spectra and infrared. As shown in Figure 6 three absorptions were observed at -7.08, 7.67 and 7.86 ppm attributed to the enolic proton (1H), the methylthio group (3H), and two methyl groups of chelate ring (6H) respectively. The percentage of enol form of IX is estimated to be above 98 %. The strong and broad band at 1576 cm^{-1} is characteristic of the carbonyl stretching vibration strongly perturbed with hydrogen bond as is seen in Fig. 7. The weak shoulder band at 1696 cm^{-1} is assigned to the carbonyl stretching of the keto form to reveal the existence of the trace of the keto tautomer. The substitution of alkylthio group increases markedly the enol ratio and results in the downfield shift of enolic proton. These facts strongly indicate that sulfur atom act

as an electron acceptor. This seems to be rather anomalous, since the S atom is usually able to conjugate through 3p orbital and consequently shows the electron donor character. The effect of sulfur will be possibly explained if we suppose the utilization of the 3d orbital of sulfur (or the hybrid orbital involving its 3s, 3p, and 3d orbitals) to accept π electrons through conjugation with the chelate ring.

The coplanarity of the substituent double bond with the chelate ring become an important factor to evaluate the effect of the substituents such as 3-alkenyl, 3-carboalkoxy, 3-nitro-, 3-acetyl, and 3-formyl derivatives on chelate ring. As one may suppose that the situation of molecular configuration is similar to 1-substituted-2,6-dimethylbenzene, there might be expected steric hindrance between the substituent and the two methyl group of chelate ring to some extent. Unfortunately a precise discussion on the coplanarity seems to be rather difficult in this stage.

Table 2 lists the observed frequencies of various double bonds of substituents and those of aliphatic (non-conjugated and conjugated) and aromatic systems as a reference.²⁸ The bands of our compounds are shifted towards lower frequencies due to the conjugation with chelate ring. This tendency seems to suggest that molecular configuration permits considerable interaction between the substituent and ring, even if the steric hindrance

inhibits complete coplanarity of the substituent with the ring.

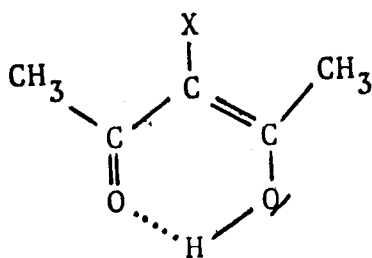
As has been reported by Burdett and Rogers,²⁹ the chemical shift of the O-H proton of some β -diketones are influenced by the concentration. Therefore, we have examined the dependencies of the concentration and used the values $\tau_{\text{O-H}}^\circ$ obtained by extrapolation of observed value $\tau_{\text{O-H}}$ to zero concentration to evaluate the strength of hydrogen bonding. Figure 8 illustrates the plot of $\tau_{\text{O-H}}^\circ$ against the concentration. Among them, the chemical shifts of the O-H of I and VI are slightly shifted to the downfield on the dilution in carbontetrachloride. The rest of them show no appreciable changes in the chemical shifts upon the dilution. It is of another interest that the enol proton of 3-substituted derivatives exhibits much sharper peak than that of acetylacetone in carbon tetrachloride at room temperature. This general observation may be explained by the absence of ethylenic proton on the 3-position, which is able to be easily exchanged with the enolic proton in high frequency.

The C=O stretching vibrations exhibit the strong and rather broad bands at around 1550-1630 cm^{-1} which are separated into the two bands upon deuteration of the enolic proton. This strong band has been interpreted as the superposition of the C=O stretching and the C=C stretching.^{5,9}

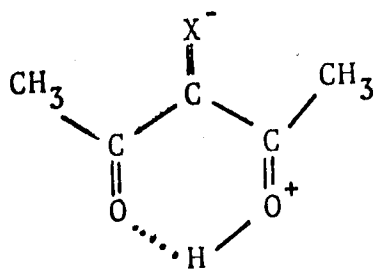
Figure 9 shows that the linear relationship exists in the plot of $\tau_{\text{O-H}}^\circ$ against the C=O stretching. It is concluded,

therefore, that the stronger hydrogen bond results in the lower frequency of the C=O stretching and the lower magnetic field of proton resonance of O-H, since the H atom is less shielded or the electron charge distribution is presumably deformed in the direction to give the lower magnetic field. Thus, it can be most likely explained the effect of the substituents on the strength of intramolecular hydrogen bond decreases in the order: $-\text{CHO} > -\text{CO}_2\text{R} > -\text{COCH}_3 > -\text{SCN} > -\text{NO}_2 > -\text{CN} > -\text{CH}=\text{CH}-\text{R} > \text{H} > \text{Cl}$. This trend can only be interpreted if we assume that (electron-withdrawing) resonance effect of the substituent on hydrogen bond is more important than the inductive effect. The resonance effect through chelate ring causes migration of the π -electron from the -OH to the substituent group, resulting in decrease of the diamagnetic shielding of the enolic hydrogen nucleus by its own electrons.³⁰ The resultant reduction of the charge density on the O-H oxygen bring the enolic proton to the closer proximity of the carbonyl oxygen to form stronger hydrogen bond and, therefore, the C=O stretching is shifted towards lower frequency region. It seems to suggest that ionic resonance form (b) contributes to a large part of the observed effects of the substituents. In contrast, it is particularly interesting to compare with the series; dibenzoylmethane, benzoylacetone, tri-fluoroacetylacetone, and hexafluoroacetylacetone, where the inductive effect give more profound influence on the chelate

ring.⁶



(a)



(b)

We obtain the value 0.037 (ppm/cm⁻¹) as the slope of the plot in Figure 9 and 0.044 for the latter case. Relatively small difference between the two values seems to indicate that substitution on the different position of chelate ring does not make so much difference in the slope of the plot, that is, the order of these values may be intrinsic to this type of chelate ring aside from the kinds of electronic effects of a substituent.

Table 1. The carbonyl stretching and the proton chemical shifts of the enol form of 3-substituted-2,4-pentanediones.

	Substituent	$\nu(\text{C=O})$ (cm^{-1})	Chemical Shift (ppm)			Enol (%)
			OH	$\text{CH}_3^a, \text{CH}_3^b$	Others**	
I	H	1623	-5.84	7.98	H(4.54s)	96
II	Cl	1618	-5.55	7.70		92
III	$-\text{CH}^a=\text{CH}^b-\text{CH}_3$	1607	-6.61	7.85	$\text{H}^a(4.09\text{m}), \text{H}^b(4.50\text{m}),$ $\text{CH}_3(8.20\text{d}; J=5.8\text{cps})$	93
IV	$-\text{CH}^a=\text{CH}^b-\text{CH}_2-\text{CH}_3$	1603	-6.60	8.00	$\text{H}^a(3.50\text{m}), \text{H}^b(4.20\text{m}),$ $\text{CH}_2(7.90\text{m})$ $\text{CH}_3(9.10\text{t}; J=7.5\text{cps})$	93
V	$-\text{CH}_2-\text{CH}=\text{CH}_2$	1606	-6.60	7.90	†	49
VI	-CN	1598	-6.90	7.58		98
VII	$-\text{NO}_2$	1595	-6.95	7.54		98
VIII	-SCN	1580	-7.10	7.48		98
IX	$-\text{SCH}_3$	1575	-7.08	7.67	$\text{CH}_3(7.86\text{s})$	98
X	$-\text{COCH}_3$	1580	-7.40	7.81	$\text{CH}_3(7.65\text{s})$	98
XI	$-\text{COOCH}_3$	1555	-7.97	7.65	$\text{CH}_3(6.25\text{s})$	98
XII	$-\text{COOCH}_2\text{CH}_3$	1560	-8.10	7.74	$\text{CH}_2(5.75\text{q}; J=7.5),$ $\text{CH}_3(8.67\text{t}; J=7.0)$	98
XIII	$-\text{CHO}^*$	1550	-8.51	7.55	H (0.03s)	98

* The values of chemical shifts are listed here for only enolic form A.

** s, d, t, and q in the parentheses denote singlet, doublet, triplet, and quartet. CH_3^a and CH_3^b indicate two methyl attached to the chelate ring.

† Assignment is difficult, because of complex splitting pattern.

Table 2. The observed frequencies of the stretching vibration of the C=O, C=C and NO₂

Substituent	Obs. Frequencies. ^a	Ref. ²⁸
$\begin{array}{c} \text{-C-CH}_3 \\ \\ \text{O} \end{array}$	1680 (cm ⁻¹)	$\nu(\text{C=O})$ { aliphatic 1725-1705 (cm ⁻¹) conjugated 1720-1670
$\begin{array}{c} \text{-C-O-C}_2\text{H}_5 \\ \\ \text{O} \end{array}$	1710	$\nu(\text{C=O})$ { aliphatic 1750-1735 conjugated -1710
$\begin{array}{c} \text{-C-O-CH}_3 \\ \\ \text{O} \end{array}$	1720	$\nu(\text{C=O})$
$\begin{array}{c} \text{-C-H} \\ \\ \text{O} \end{array}$	1677	$\nu(\text{C=O})$ { aliphatic 1740-1720 conjugated 1685-1664 aromatic 1710-1695
-NO ₂	{ 1530 1350	$\nu_{\text{as}}(\text{NO}_2)$ { aliphatic { ν_{as} 1556-1545 ν_{s} 1390-1355
		$\nu_{\text{s}}(\text{NO}_2)$ { conjugated { ν_{as} 1550-1500 ν_{s} 1360-1290
		$\nu_{\text{s}}(\text{NO}_2)$ { aromatic { ν_{as} 1530-1500 ν_{s} 1370-1330
-CH=CH-CH ₃	1607	$\nu(\text{C=C})$ conjugated 1630-1600
-CH ₂ -CH=CH ₂	1640	mono olefine 1650

(a) ν_{s} and ν_{as} denote the symmetric stretching and antisymmetric stretching of the NO₂ respectively. Observed frequencies were calibrated from the polyethylene film.

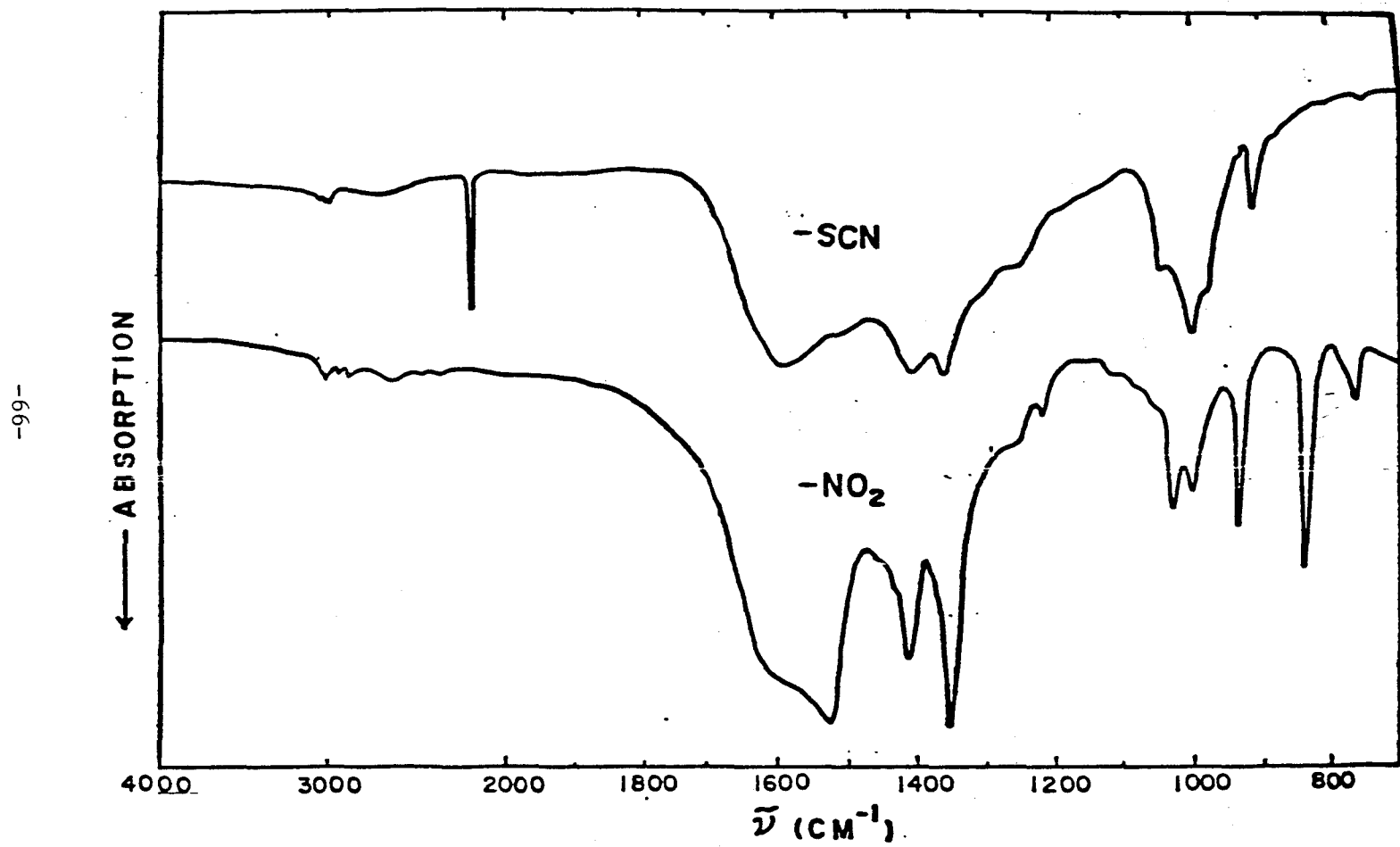


Fig. 1 Infrared spectra of 3-nitro-2,4-pentanedione and 3-thiocyano-2,4-pentanedione.

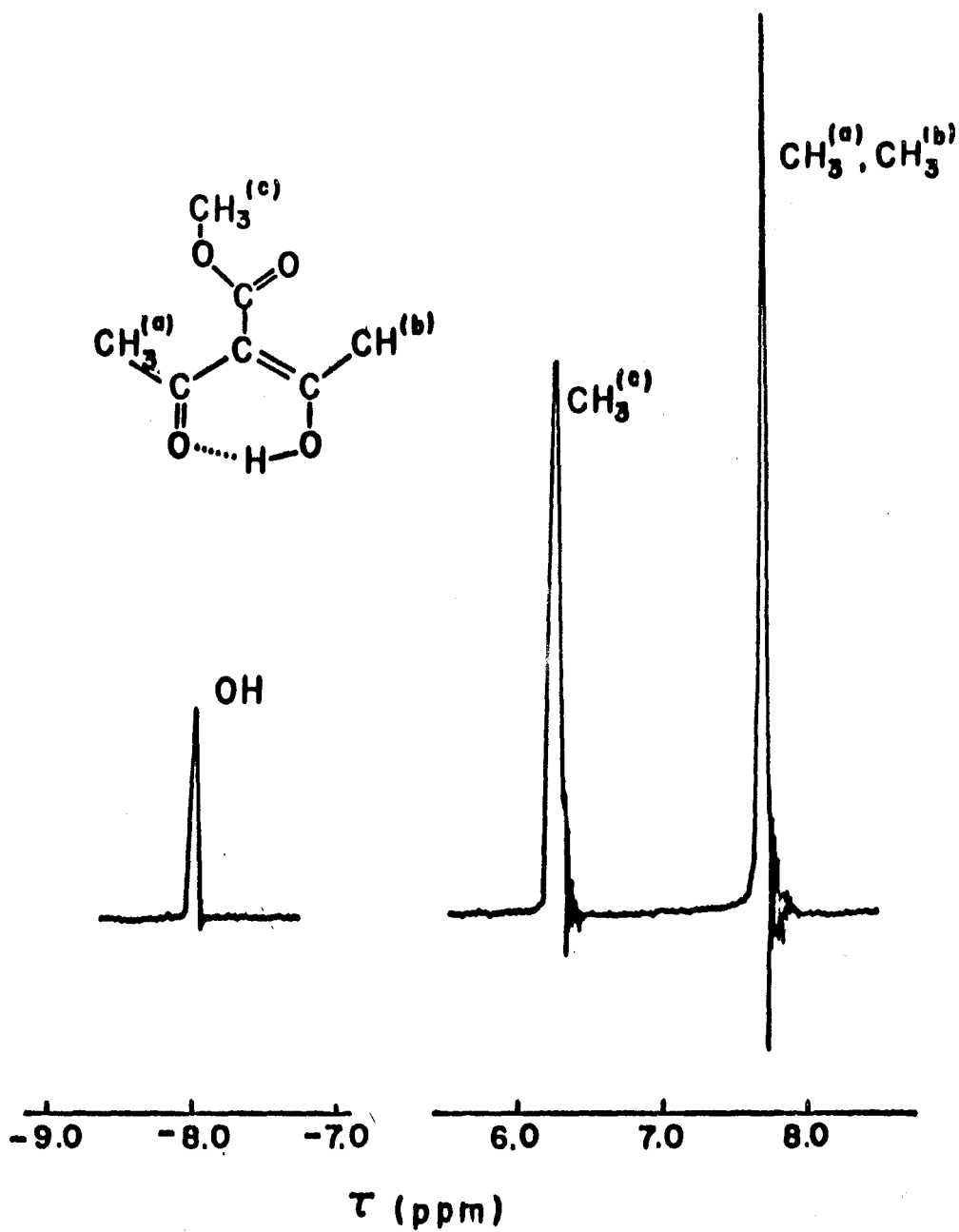


Fig. 2 NMR spectrum of 3-carbomethoxy-2,4-pentanedione

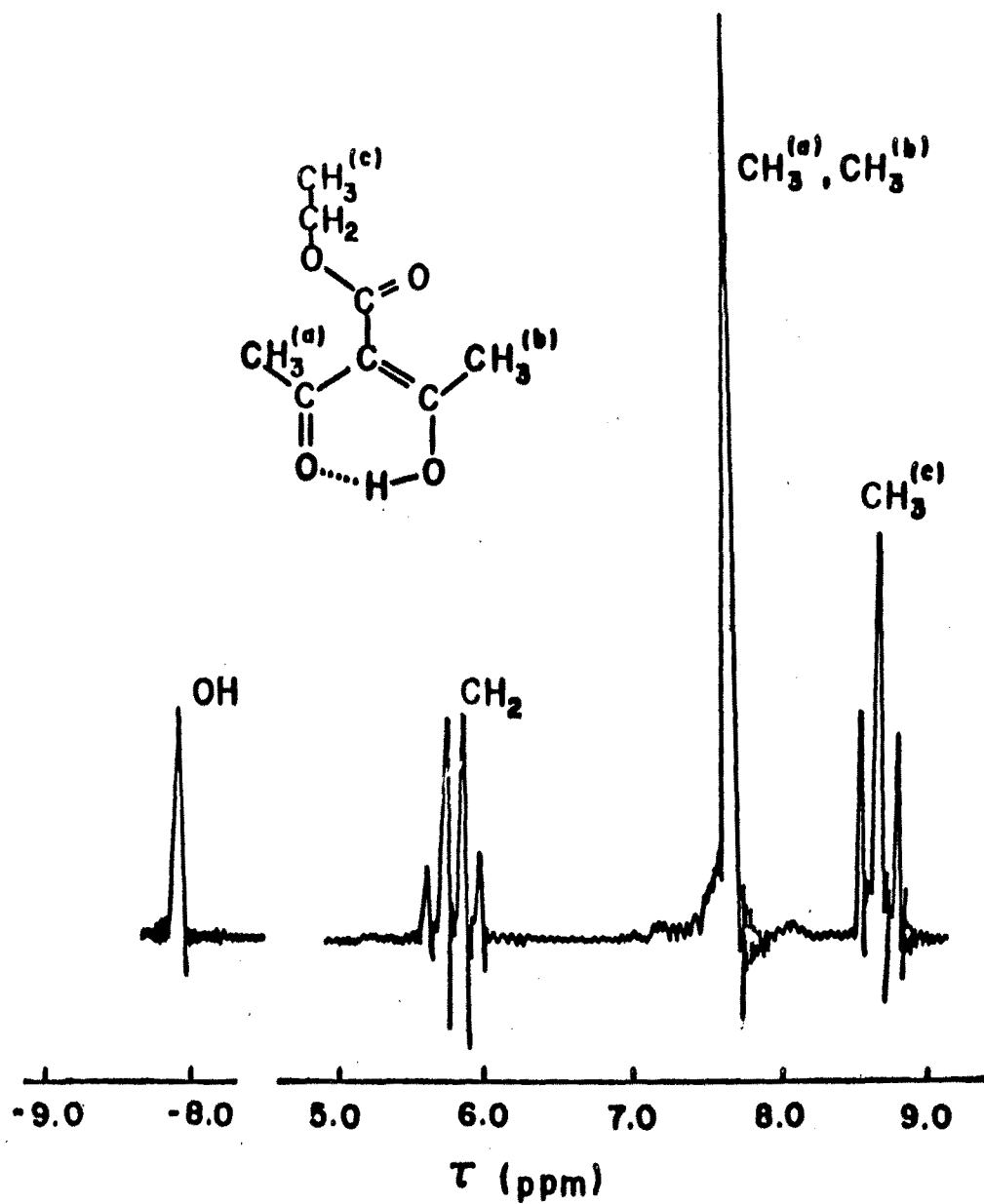


Fig. 3 NMR spectrum of 3-carboethoxy-2,4-pentanedione

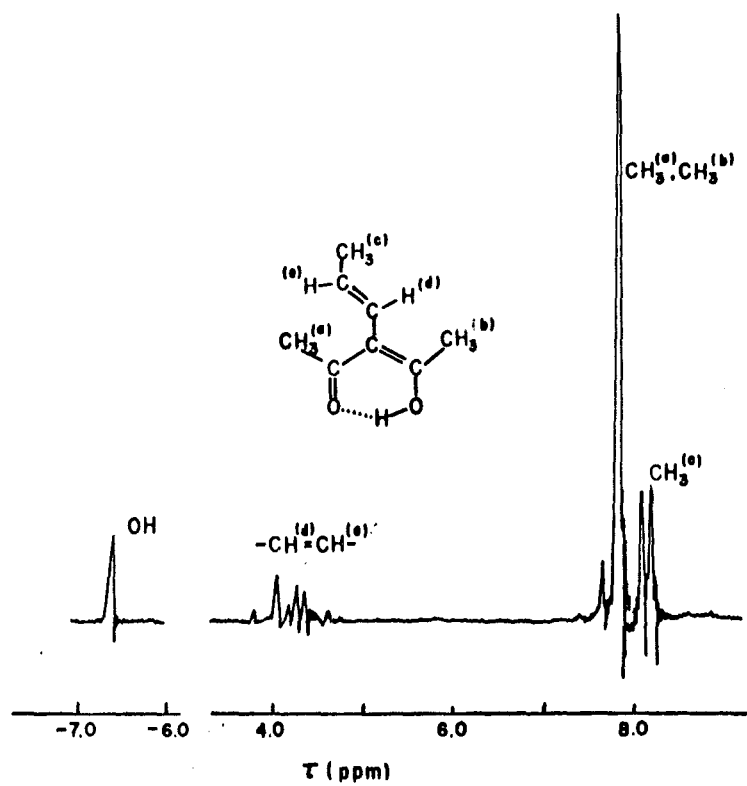


Fig. 4. NMR spectrum of 3-propenyl-2,4-pentanedione

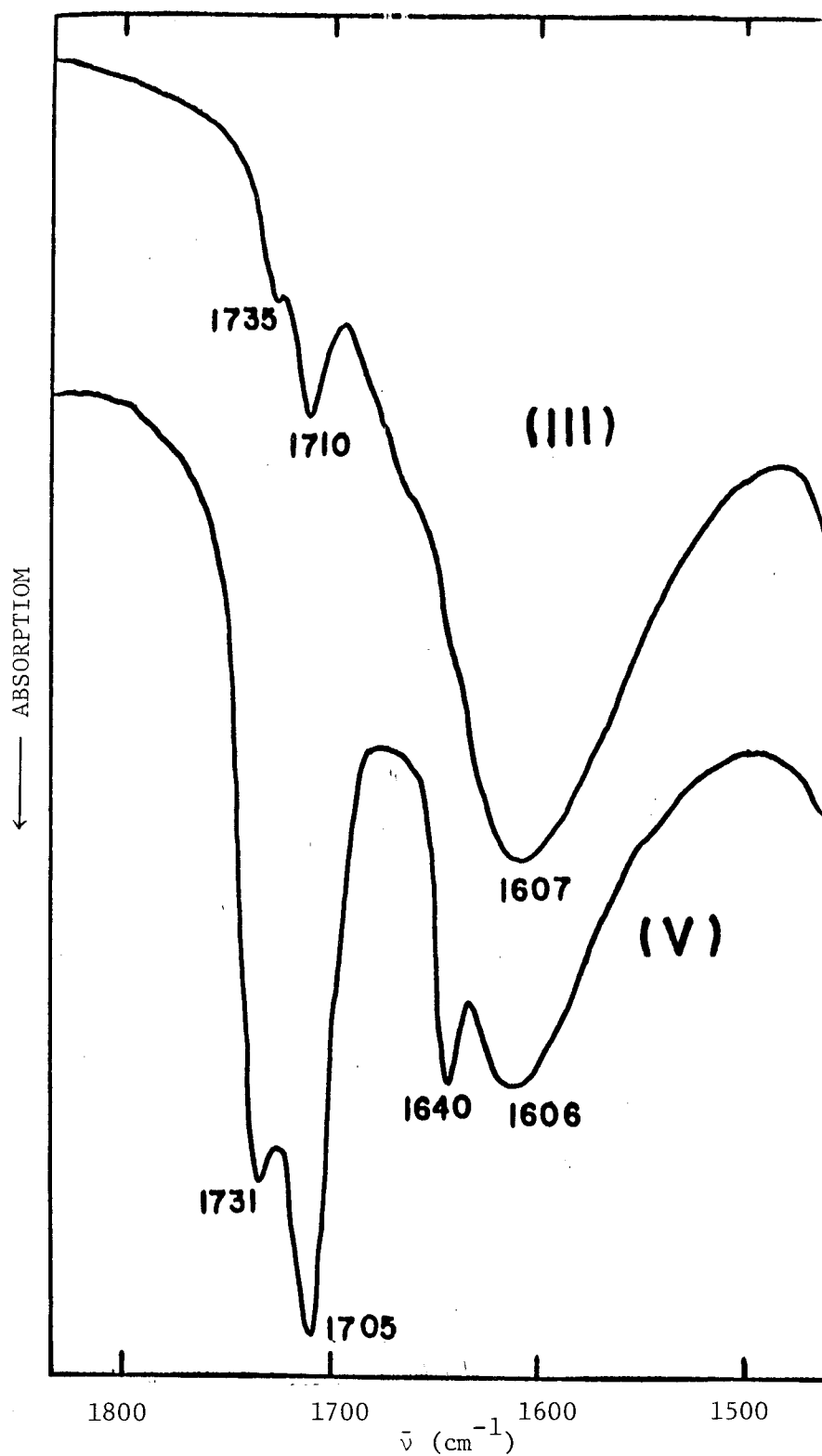


Fig. 5 Infrared spectra of 3-propenyl-2,4-pentanedione (III)₋₁ and 3-allyl-2,4-pentanedione (V) from 1800 to 1500 cm^{-1}

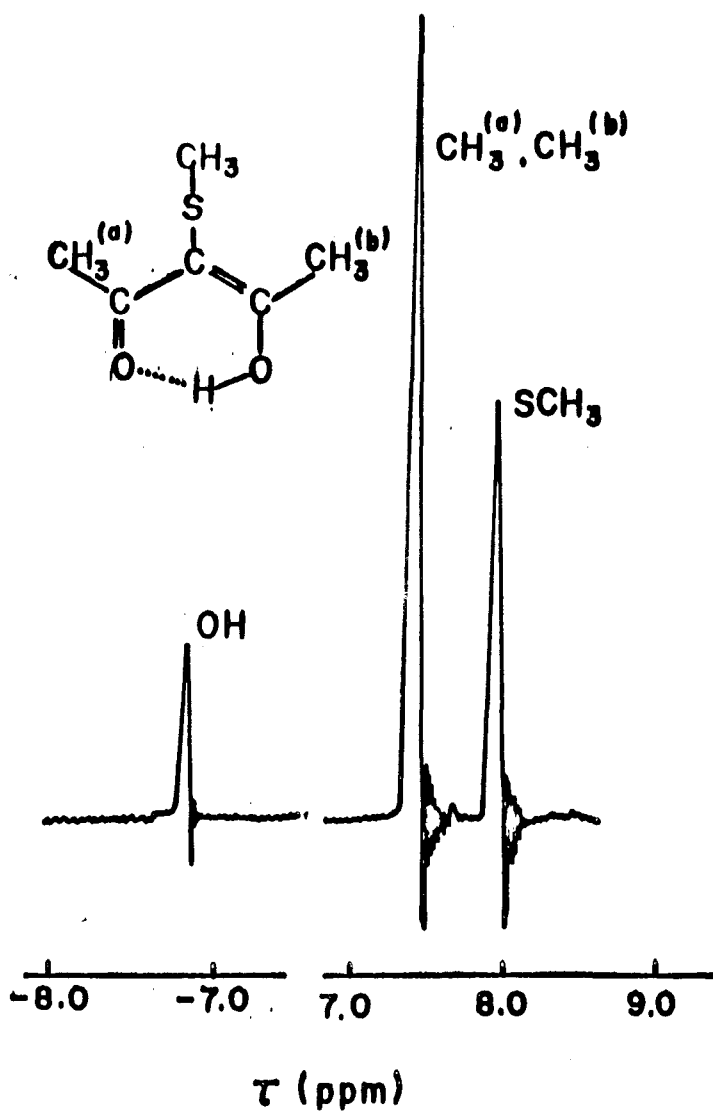


Fig. 6 NMR spectrum of 3-methylthio-2,4-pentanedione

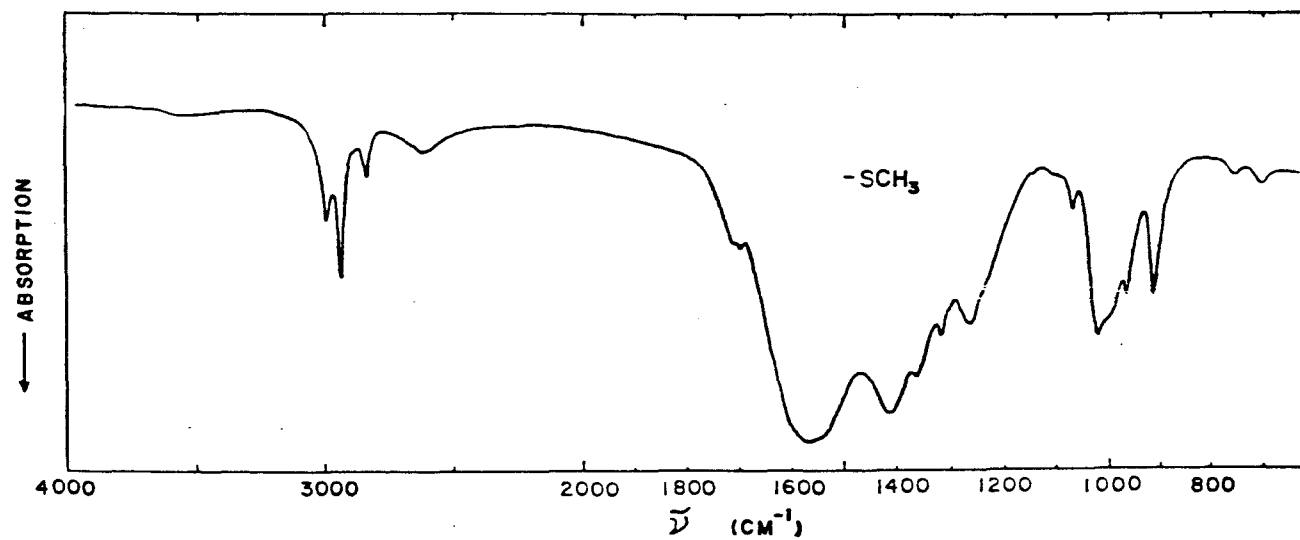


Fig. 7 Infrared spectrum of 3-methylthio-2,4-pentanedione

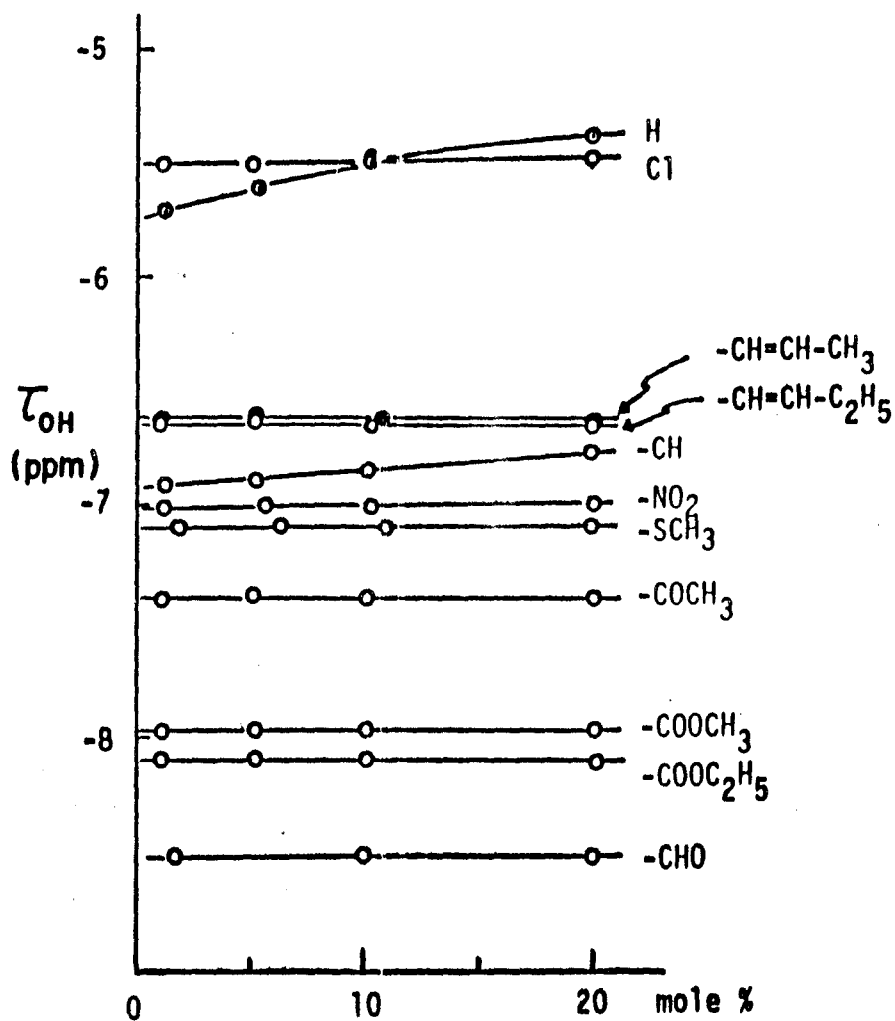


Fig. 8 Chemical shift (τ_{OH}) of the OH proton as a function of the concentration of 3-substituted-2,4-pentanediones in carbon tetrachloride

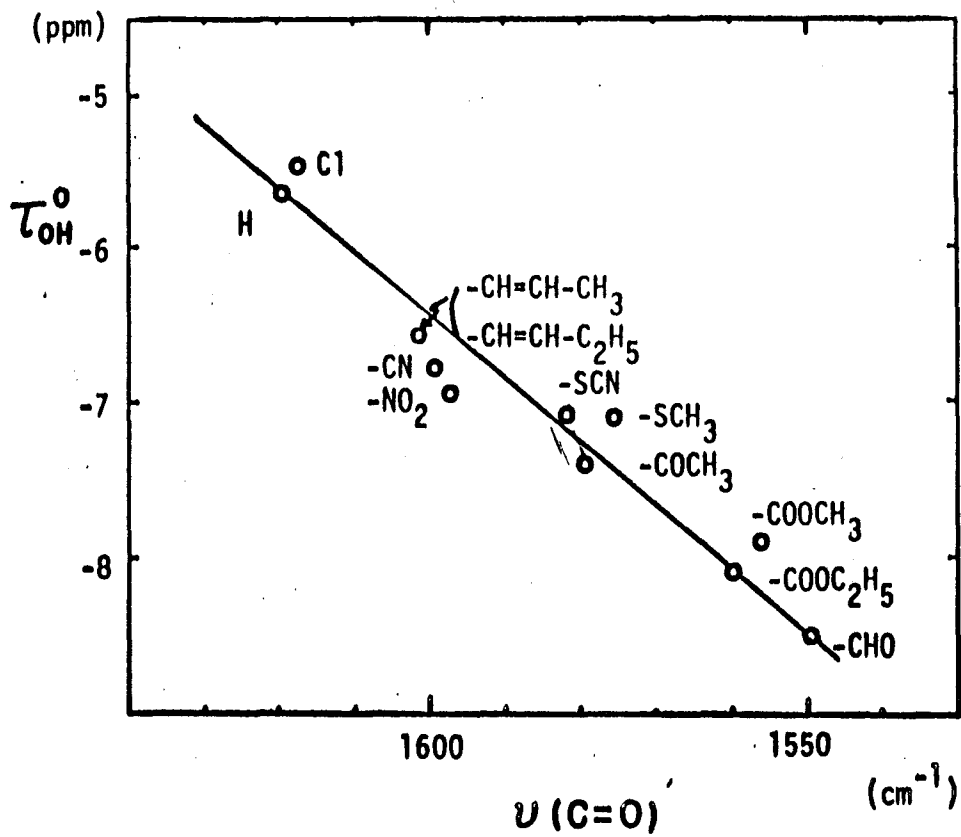


Fig. 9 Plot of chemical shift (τ_{OH}^0) of OH proton at infinite dilution against C=O stretching frequency

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Chapter 4

Synthesis and Structural Elucidation of α -Alkylthio- and α -Phenylthio- β -dicarbonyls.*¹

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*¹ Presented in part at the 21 Annual Meeting of the Chemical Society of Japan at Osaka, April, 1968.

4.1 Summary

Various α -alkylthio- and α -phenylthio- β -dicarbonyls have been prepared by the reaction of α -chloro- β -dicarbonyls with mercaptans in the presence of pyridine or piperidine and their structures have been established. It was found that an introduction of alkylthio and phenylthio group into α -position of β -dicarbonyls resulted in marked shift of the tautomeric equilibrium to enol side. The enhanced stability of the chelate ring involving strong hydrogen bonding is explained in terms of the electron withdrawing resonance effect of divalent sulfur atom from the chelate ring through $p\pi-d\pi$ conjugation.

4.2 Introduction

Several works in which α -hydrogen of the active methylene group have been substituted with alkylthio or phenylthio groups by the usual electrophilic substitution have been reported. Thus, α -alkylthio and α -arylthio- β -dicarbonyls have been prepared by the reaction of β -dicarbonyls with α -chloroethylsulfenyl chloride,¹ vinylsulfenyl chloride,¹ acetylsulfenyl chloride,² o-nitrobenzenesulfenyl chloride,³ 2,4-dinitrobenzenesulfenyl chloride.³ However, no precise structural studies and behavior at tautomeric equilibrium are known for these compounds. In another synthetic approach to form the C-S linkage at the α -position, nucleophilic substitution was proposed as the possible course of the reaction of

diethyl bromomalonate with ethylmercaptan by Waygand.⁴ The latter reaction are of particular interest to us because they proved easier alternative synthetic pathway for α -alkylthio and α -phenylthio- β -dicarbonyls.

Further, there have been several discussions^{5,6,7,8,9} on the subject that the conjugation of the sulfur atom directly attached to an adjacent double bond involves the 3p or 3d orbitals of sulfur. However, systematic work has not been done for α -alkylthio- and α -phenylthio- β -dicarbonyls so far.

Such work has been indicated here as an example by which resolve questions regarding the conjugative interaction of sulfur with intramolecularly hydrogen bonded chelate rings and its effect on the tautomeric equilibria.

4.3 Experimental

Melting points were determined on Kyoto Electronic Co., apparatus and were uncorrected. Infrared spectra were measured on Jasco DG-402G spectrophotometers in carbon tetrachloride solution calibrated by polystyrene film. The mmr spectra were recorded on Jeolco JNM-C-60H spectrophotometers using TMS as an internal reference. The ultraviolet spectra were determined in n-heptane on Hitachi Model EPS-3T spectrophotometer.

Starting Materials

3-Chloro-2,4-pentanedione was prepared by the method of

Suzuki.¹⁰ Ethyl and methyl α -chloro acetoacetate were prepared by chlorination of the corresponding ketoesters with sulfenyl chloride.¹⁰ 1-Phenyl-2-chloro-3-butanedione was prepared from benzoylacetone and sulfenyl chloride following the method of Stenner.¹¹ 1-3-Diphenyl-2-chloro-propanedione was prepared from benzoylacetone and sulfenyl chloride.¹² All mercaptans obtained from commercial source were dried and distilled before their uses.

General Procedure for Method A.
(represented by (I))

To the solution of 7.0 g (0.057 mole) of 3-chloro-2,4-pentanedione and 3.5 g (0.057 mole) of ethylmercaptan was slowly added 5.0 g (0.063 mole) of pyridine under vigorous stirring at room temperature for 30 min., followed by further stirring for 6 hr. Precipitated pyridine hydrochloride was filtered off and washed with three portions of 20 ml of ethylether. Combined filtrates was washed with 30 ml of water five times and dried over anhydrous sodium sulfate. A solvent was removed under reduced pressure using rotary evaporator. Crude product was purified by distillation. Four compounds, (VI), (VII), (VIII), and (XI) were recrystallized from n-hexane. (IX) and (XIII) were recrystallized from benzene-methanol mixture to give needle crystals.

General Procedure for Method B
(represented by (II))

A solution of 13.4 g of (0.10 mole) of 3-chloro-2,4-pentanedione, 10 g (0.12 mole) of pyridine, and 8.4 g (0.11 mole) of iso-propylmercaptan in 15 ml of carbon tetrachloride was refluxed under vigorous stirring for 10 hr. Subsequent procedure was identical with method A.

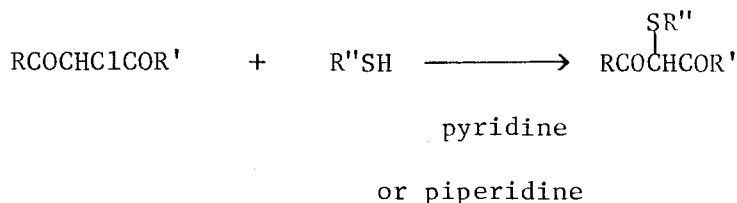
General Procedure for Method C
(represented by (III))

To a solution of 37.4 g (0.28 mole) of tert-butylmercaptan and 37.5 g (0.28 mole) of 3-chloro-2,4-pentanedione cooled at 0°C was added dropwisely 23.0 g (0.27 mole) of piperidine in 20 ml of chloroform for 10 min. After exothermic reaction ceased, the reaction mixture was added by 100 ml of methyl alcohol followed by further stirring for 5 hr at room temperature. Successive treatment was identical with method A. (X) and (XIV) were recrystallized from ether solution.

4.4 Results and Discussion

Our first attempts to prepare α -alkylthio and α -phenylthio- β -dicarbonyls have been done through the reaction of relatively stable α -chloro- β -dicarbonyls with various mercaptans in the presence of pyridine or piperidine. The results are listed in Table I. The reaction conditions were varied depending on the reactivity of mercaptans. When α -chloro- β -dicarbonyls were

treated with the thiophenol or ethylmercaptan in the presence of pyridine, an exothermic reaction occurred



beta-dicarbonyls: $\text{CH}_3\text{COCH}_2\text{COCH}_3$, $\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$, $\text{CH}_3\text{COCH}_2\text{CO}_2\text{CH}_3$,
 $\text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3$, $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$

mercaptans: alkylmercaptans, $\text{C}_6\text{H}_5\text{SH}$, $\text{HSCH}_2\text{CH}_2\text{SH}$, HSCH_2COOH

with the immediate precipitation of pyridinium hydrochloride even at room temperature. However more drastic conditions were required as a size of the alkyl group on the mercaptan was increased. Higher temperature and longer reaction periods were necessary to effect a reaction with i-propylmercaptan. For the reaction with t-butylmercaptan or n-butylmercaptan using pyridine in carbon tetrachloride, only small amounts of the hydrochloride salt were found after refluxing for 24 hours. On the other hand, the use of piperidine accelerated the reactions without warming. As a matter of fact, these reactions can be effectively controlled by prefer choice of the basicity of the amine and acidity of the mercaptan.

The structure and tautomeric ratio were determined from analyses and spectroscopic properties. The chemical shifts of

synthesized α -alkylthio- and α -phenylthio- β -dicarbonyls in carbon tetrachloride solution are listed in Table II. In the nmr spectra, the chemical shifts of enol proton appeared at lower magnetic field, in the region $-6 \sim -8$ ppm for β -diketones and $-2 \sim -4$ ppm for β -ketoesters are ascribed to intramolecularly hydrogen bonded proton.¹³ The highly enolized structures except for 1,3-diphenyl-2-phenylthio-1,3-propanedione (VII) and 1,3-diphenyl-2-methylthio-1,3-propanedione (VIII) are confirmed by the absence of signals of -CHX- together with intensity ratios of the enol proton to the protons of R and R' group.

Table III lists UV spectra in n-heptane and the prominent vibrational frequencies of the chelate ring with the tentative assignments according to normal coordinate analyses.¹⁴ A weak and broad absorption at around 2600 cm^{-1} for β -diketones and a band at $2700\text{--}2900\text{ cm}^{-1}$ for β -ketoesters are assigned to strongly hydrogen bonded O-H stretching vibrations. A strong and broad absorption at $1580\text{--}1560\text{ cm}^{-1}$ in β -diketones is attributed to the C=O stretching vibration strongly perturbed by hydrogen bonding and superimposed with the C=C stretching vibration. This composite band is shifted by about $60\text{--}80\text{ cm}^{-1}$ toward lower frequency region compared with the original β -diketones.

Two strong absorptions at $1640\text{--}1620$ and $1590\text{--}1670\text{ cm}^{-1}$ can be assigned to the C=O and the C=C stretching for the chelate ring of β -ketoesters respectively.^{15,16,17,18} Since $\nu(\text{C=O})$

and $\nu(\text{C}=\text{C})$ appear at 1655 and 1632 cm^{-1} in ethyl acetoacetate, it indicates that a stronger intramolecular hydrogen bond and more delocalization of π -electrons in the chelate ring are formed by substitution with an alkylthio or phenylthio group. These trends are consistent with what we observed in the nmr spectra. For α -substituted β -ketoesters, very weak absorption at 1720 cm^{-1} due to free carbonyl stretching indicates the existence of trace amounts of the keto form which could not be observed in the nmr spectrum.

Reactions of 3-chloro-2,4-pentanedione or ethyl α -chloro acetoacetate with dithioethyleneglycol afforded respectively (IX) and (XIII) as colorless crystals in moderate yields. These two compounds exhibit the characteristic infrared spectra of chelation as are shown in Table III. The keto forms are excluded by the absence of $\nu(\text{C}=\text{O})$ due to the free carbonyl stretching. The singlet enol proton and identical signals of R or R' belonged to the different chelate rings suggest the dienolic structure consisted of the two equivalent chelate rings as shown in Figure 1. (VII) and (VIII) were confirmed to be complete keto form both in crystals and non polar solvents by the appearance of chemical shift of $-\overset{|}{\text{CH}}-$ and three strong absorptions at around 1720 cm^{-1} due to free carbonyl stretchings. It is presumed that a strong steric interaction between the sulfur atom and the two phenyls attached to the chelate ring destabilize chelate ring resulting

in considerable loss of coplanarity of two phenyl rings to chelate ring and giving more stable keto tautomer. In contrast, in case of 1-phenyl-2-phenylthio-1,3-butanedione (VI) one phenyl ring attached to chelate ring can permit (VI) to form enol structure, even if there is an interaction between sulfur atom and phenyl ring to some extent. Its nmr spectrum is demonstrated in Fig. 2.

Ultraviolet spectra showed characteristic absorption at 280-300 m μ for β -diketones¹⁹ and about 250 m μ for β -ketoesters²⁰ as shown in Table III. These bands are assigned to the first $\pi \longrightarrow \pi^*$ transition of chelate ring involving the intramolecular hydrogen bond. α -Alkylthio- β -diketones exhibits absorption at around 230 m μ ($\epsilon=1,500-2,000$) which has not been observed in other α -substituted β -diketones such as nitro, cyano, acetyl and chloro.²¹ At the present time, it can not be determined whether this band is attributed to the excitation of non-bonding electrons of sulfur to the higher level involving 3d orbitals of sulfur and chelate ring without precise molecular orbital calculations and these are currently being made in our laboratory.

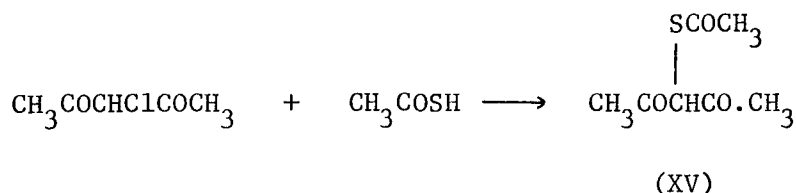
It is of interest to compare the ratio of tautomers in the α -substituted- β -ketoesters with those of their non substituted β -ketoesters.²² By contrast with β -diketones, it is noteworthy that α -thio substituted β -ketoesters (XI), (XII), and (XIII) cause surprising shift of tautomeric equilibrium to the enol side relative to parent β -ketoesters. Figure 3 shows the nmr spectra

of α -phenylthio- β -ketoesters.

Furthermore, similar treatment of α -chloro- β -dicarbonyls with thioglycolic acid gave 3-carboxymethylthio-2,4-pentanedione (X) and methyl α -carboxymethylthio-acetoacetate (XIV). Figure 4 shows the nmr spectra of (X) and (XIV) in CDCl_3 with TMS as an internal standard. Broadened singlets at τ 0.18 for (X) and τ 1.22 for (XIV) are assigned to carboxy proton according to the dependency of their chemical shifts upon dilution. On the contrary, sharp singlets at τ -7.62 of (X) and τ -3.52 of (XVI) assigned to enolic proton are slightly sensitive to dilution. This fact indicates that the strong intramolecular hydrogen bond results in slower inter and intramolecular proton exchange compared with carboxy proton. Figure 5 shows the dependencies of two proton signals on dilution.

The infrared spectra of (X) exhibited a strong band at 2960 cm^{-1} and 1700 cm^{-1} owing to bonded O-H and the carbonyl stretching of carboxy group respectively as is seen in Figure 6. The broad and strong absorption at 1570 cm^{-1} shows a good evidence to support the chelate ring structure. The infrared spectrum of (XIV) in Figure 7 is akin to that of (X).

It is also noticed that this reaction route is able to extend to prepare 3-acetylthio-2,4-pentanedione (XV) by using 3-chloro-2,4-pentanedione and thioacetic acid in stead of 2,4-pentanedione and acetylsulphenylchloride.¹



Complete enolization of (XV) was confirmed by proton signals at 7.86, 7.67, and -7.29 with intensity ratios of 6:3:1 in Fig. 8.

In comparison with the parent β -dicarbonyls, chemical shift of enol proton resonates at lower magnetic field and the C=O stretching shifts toward lower frequency region as increasing the strength of hydrogen bond. Accordingly, it is clearly indicated that substitution with alkylthio or phenylthio group results in formation of stronger hydrogen bond and more delocalization of π -electrons in chelate ring.

In connection with the effect of α -substituents on tautomeric equilibria and hydrogen bonding, the few works have been reported to give rather vague conclusions.^{23,24} We have suggested that the major effect of α -substituents may be attributed to mesomeric effect and electron-withdrawing group such as nitro, acetyl, and cyano will increase delocalization of electrons in the chelate ring and the strength of the hydrogen bonding.²¹ As has been pointed out by Baker and Harris,⁸ sulfur in thioesters directly attached to the carbonyl participates in resonance interaction in the ground state through its 3d orbitals. Thus it may be analogously considered that the sulfur atom directly attached to

the α -position of β -dicarbonyls behaves as an electron-withdrawing substituent through $p\pi-d\pi$ conjugation rather than electron-releasing at ground state. This leads to reasonable conclusion that the decrease of electron density on the enol oxygen favors shift of the proton at the equilibrium position closer to the oxygen of carbonyl, forming a stronger hydrogen bond. High enolization can be also explained by the decrease of the electron density on methylene carbon to cause easier proton releasing relative to the parent β -dicarbonyls.

Table I Synthetized α -Alkylthio- and α -Phenylthio- β -dicarbonyls, RCOCHXCOR'

Compound	R	R'	X	yield ^a (%)	Bp(mm), °C	Formula	Calcd., (%)			Found, (%)			Method of Preparation
							C	H	S	C	H	S	
I	CH ₃	CH ₃	SC ₂ H ₅	84	95(20)	C ₇ H ₁₂ O ₂ S	52.45	7.55	20.00	52.47	7.70	19.93	A
II	CH ₃	CH ₃	S(1-C ₃ H ₇)	46	87-88(8)	C ₈ H ₁₄ O ₂ S	55.10	8.10	18.36	55.31	8.14	18.10	B
III	CH ₃	CH ₃	S(t-C ₄ H ₉)	63	68-70(7)	C ₉ H ₁₆ O ₂ S	57.40	8.56	17.01	57.65	8.84	16.71	C
IV	CH ₃	CH ₃	S(n-C ₄ H ₉)	44	80-81(9)	C ₉ H ₁₆ O ₂ S	57.40	8.56	17.01	57.70	8.69	17.25	C
V	CH ₃	CH ₃	SC ₆ H ₅	81	142-143(12)	C ₁₁ H ₁₂ O ₂ S	63.19	6.08	15.54	63.46	5.81	15.40	A
VI	C ₆ H ₅	CH ₃	SC ₆ H ₅	40	63 ^b	C ₁₆ H ₁₄ O ₂ S	71.08	5.21	11.85	71.45	5.27	11.95	A
VII	C ₆ H ₅	C ₆ H ₅	SC ₆ H ₅	32	33-34 ^b	C ₂₁ H ₁₆ O ₂ S	75.87	4.85	9.64	75.87	4.84	9.60	A
VIII	C ₆ H ₅	C ₆ H ₅	SCH ₃	36	88 ^b	C ₁₆ H ₁₄ O ₂ S	71.08	5.21	11.85	70.84	5.19	11.71	A
IX	CH ₃	CH ₃	SCH ₂ CH ₂ S	83	126-127 ^b	C ₁₂ H ₁₈ O ₂ S ₂	49.85	6.32	22.09	49.51	6.42	21.82	A
X	CH ₃	CH ₃	SCH ₂ COOH	45	86	C ₇ H ₁₀ O ₄ S	44.20	5.26	16.86	43.93	5.28	16.61	C
XI	CH ₃	OCH ₃	SC ₆ H ₅	45	35 ^b	C ₁₁ H ₁₂ O ₃ S	58.91	5.39	14.30	58.82	5.27	14.14	A
XII	CH ₃	OC ₂ H ₅	SC ₆ H ₅	53	165(19)	C ₁₂ H ₁₄ O ₃ S	60.48	5.92	13.46	60.46	5.94	13.78	A
XIII	CH ₃	OC ₂ H ₅	SCH ₂ CH ₂ S	65	106 ^b	C ₁₄ H ₂₂ O ₆ S ₂	48.00	6.29	18.30	48.08	6.41	18.10	A
XIV	CH ₃	OCH ₃	SCH ₂ COOH	38	82	C ₇ H ₁₀ O ₅ S	41.05	4.85	15.55	40.78	4.87	15.27	C

a) yields based on β -dicarbonyl

b) melting points.

Table II Nuclear Magnetic Resonance Spectra^a

Compound	R	R'	OH	R''
I		7.60 s (CH ₃)	-6.96 s	7.80 t (-SCCH ₃), 7.50 m (-SCH ₂ C)
II		7.70 s (CH ₃)	-7.17 s	8.80 d (-SC(CH ₃) ₂), 7.70-7.50 m (-SCH)
III		7.72 s (CH ₃)	-7.39 s	8.80 s (-SC(CH ₃) ₃)
IV		7.71 s (CH ₃)	-7.17 s	8.60 m (-SCCH ₂ CH ₂ C), 7.41 t (-SCH ₂ -), 8.90 t (-SCCCH ₃)
V		7.72 s (CH ₃)	-7.33 s	2.90 s (-SC ₆ H ₅)
VI	2.94 s (-C ₆ H ₅)	7.70 s (CH ₃)	-7.75 s	3.11-3.15 m (-C ₆ H ₅)
VII	2.30 m (two C ₆ H ₅)		-----	2.90 m (-SC ₆ H ₅), 4.37 s (-CH-)
VIII	2.40 m (two C ₆ H ₅)		-----	7.95 s (-SCH ₃), 4.66 s (-CH-)
IX	7.65 s (CH ₃)		-6.52 s	7.34 s (-SCH ₂ CH ₂ S-)
X	7.57 s (CH ₃)		-7.20 s	6.76 s (-SCH ₂ -CO-), 0.18 s (COOH)
XI	7.78 s (CH ₃)	6.45 s (OCH ₃)	-3.66 s	3.16-3.20 m (-SC ₆ H ₅)
XII	7.80 s (CH ₃)	6.20 q (-OCH ₂ C), 8.90 t (-OCCH ₃)	-3.73 s	3.18-3.19 m (-SC ₆ H ₅)
XIII	7.74 s (CH ₃)	8.69 t (-OCCH ₃), 5.88 q (-OCH ₂ C)	-2.95 s	7.48 s (-SCH ₂ CH ₂ S-)
XIV	7.64 s (CH ₃)	6.19 s (-OCH ₃)	-3.52 s	6.74 s (-SCH ₂ CO-), 1.22 s (COOH)

a) measured from TMS as an internal reference in CCl₄. b) s, d, t, and q denote singlet, doublet, triplet, quartet, and multiplet, respectively.

Table III IR and UV spectra for α -alkylthio- and α -phenylthio- β -dicarbonyls

Compound	IR Spectra (cm^{-1}) ^{a)}			UV Spectra ^{b)}	
	$\nu(\text{O-H})$	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\lambda_{\text{max}}, \mu\text{m} (\log \epsilon_{\text{max}})$	
I	2590		1578 ^{c)}	203(3.81), 234(3.08), 287(3.93)	
II	2596		1582 ^{c)}	203(3.81), 234(3.08), 288(3.86)	
III	2600		1565 ^{c)}	203(3.84), 230(3.17), 289(3.87)	
IV	2600		1575 ^{c)}	203(3.81), 230(3.00), 289(3.90)	
V	2580		1572 ^{c)}	207(4.42), 249(4.17), 279(3.95)	
VI	2510		1525 ^{c)}	252(4.25), 298(4.06) ^{e)}	
VII		1710,	1679, 1663 ^{d)}	198(4.17), 252(4.29), 290(3.48)	
VIII		1709,	1671, 1659 ^{d)}	198(4.17), 246(4.30), 285(3.60)	
IX	2570		1575	203(4.13), 232(3.40), 286(4.17)	
X	— ^{f)}		1570	285(3.89) ^{e)}	
XI	2780	1624	1590	198(4.23), 250(4.17), 297(3.30)	
XII	2780	1625	1589	197(4.23), 250(4.24), 300(3.35)	
XIII	2880	1638	1572	215(4.04), 250(4.25), 286(3.90)	
XIV	— ^{f)}	1639	1572	249(3.84), 278(3.48) ^{e)}	

a) measured in CCl_4 , b) measured in n-heptane, c) overlapped with $\nu(\text{C=O})$ and $\nu(\text{C=C})$

d) $\nu(\text{C=O})$ for ketoform, e) measured in CHCl_3 , f) difficult assignment due to the superimposition

of $\nu(\text{OH})$ of the COOH .

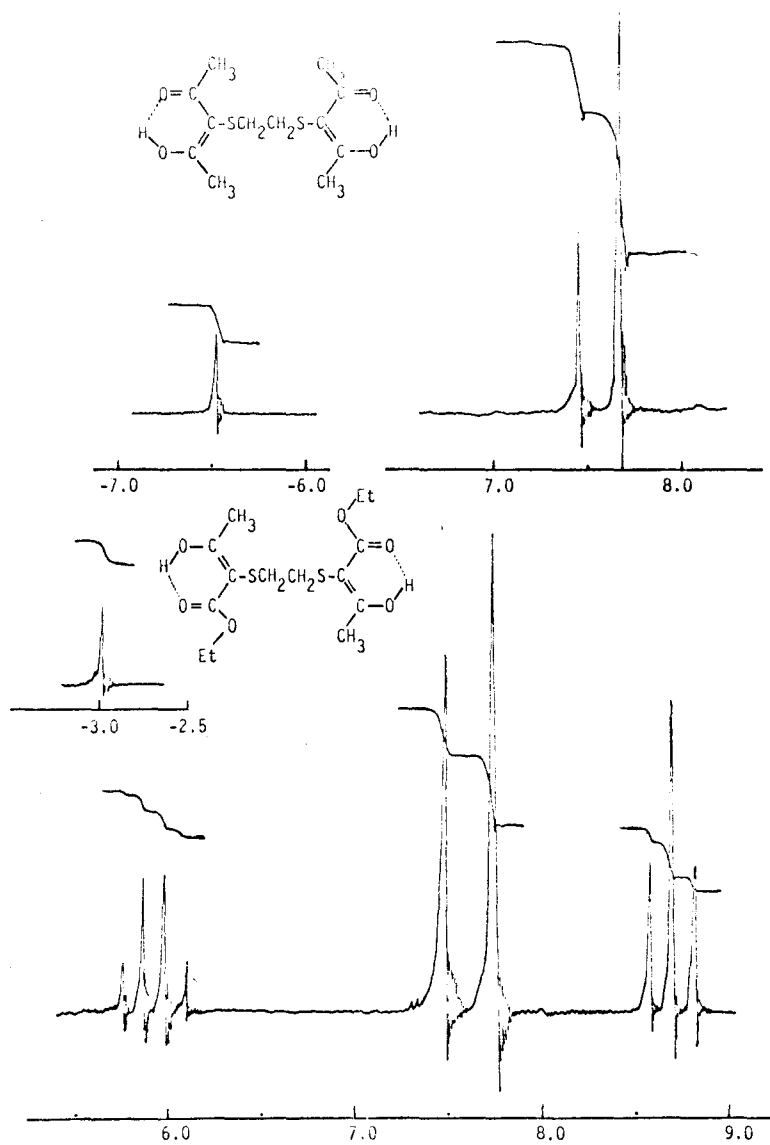


Figure 1 The NMR spectra of ethylenebis-(3-thio-2,4-pentane-dione) (IX) and ethylenebis-(ethyl α -thioaceto-acetate) (XIII)

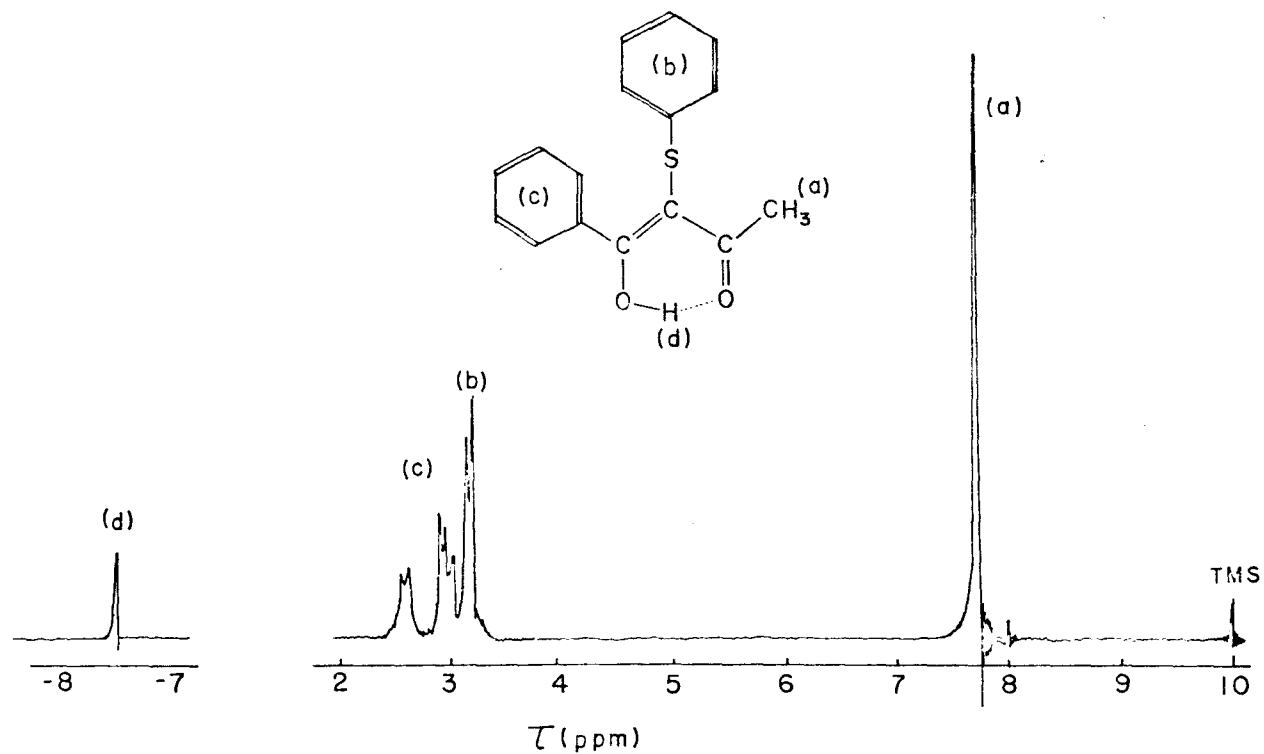
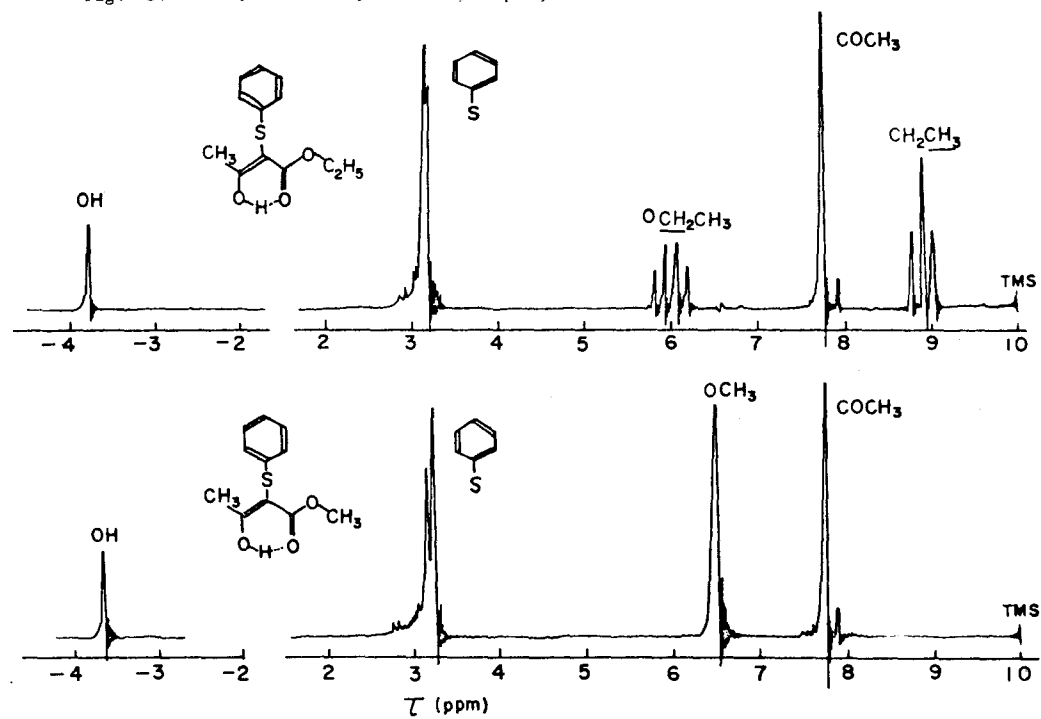


Fig. 2 The nmr spectrum of 3-phenylthio-1-phenyl-1,3-butanedione.

Fig. 3. Nmr spectra of Ethyl and Methyl α -phenylthio acetoacetate



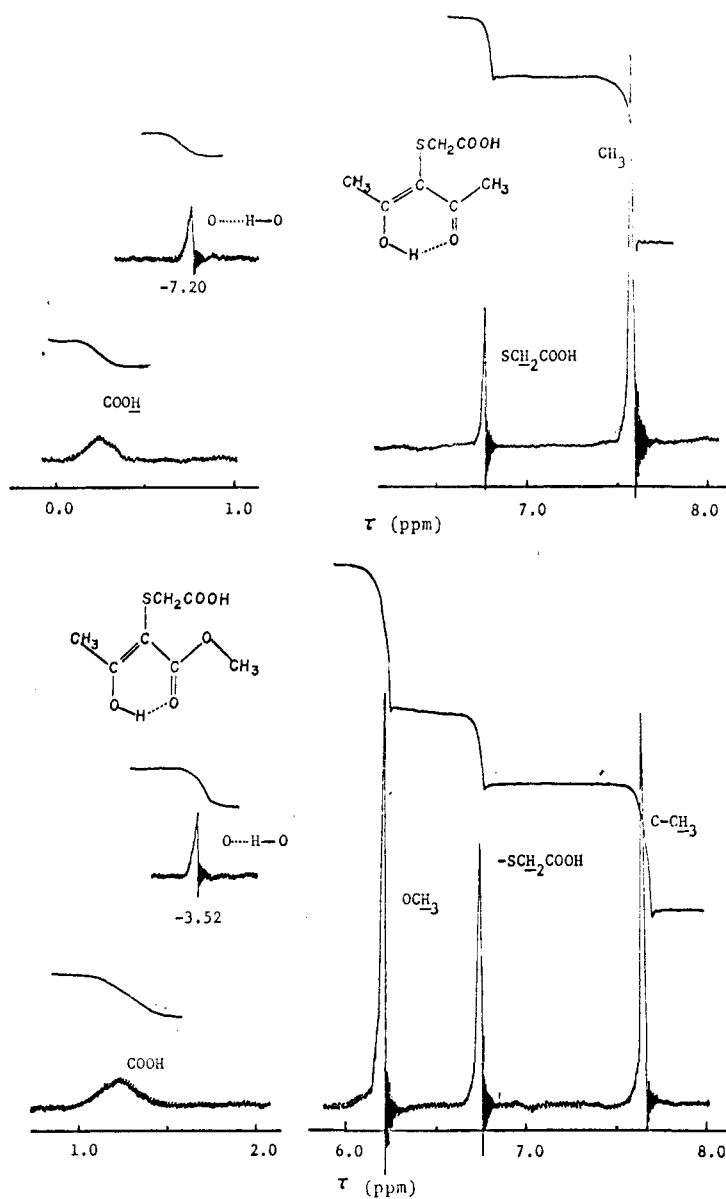


Figure 4 The NMR spectra of 3-carboxymethylthio-2,4-pentanedione (X) and methyl α -carboxymethylthioacetate (XIV)

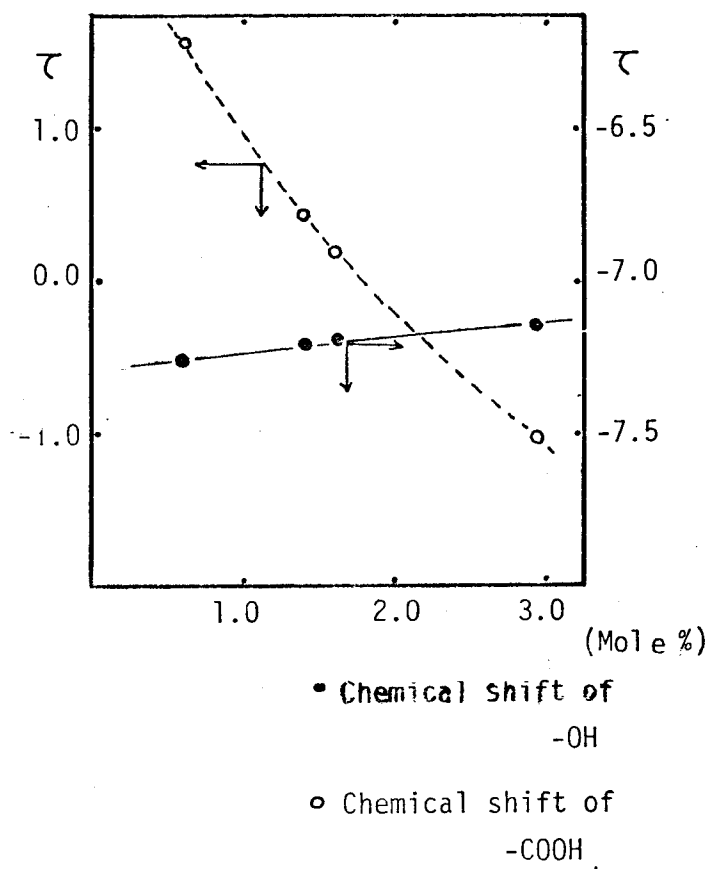


Fig. 5 The dependencies of chemical shifts of the -COOH and O-H of (X) on dilution.

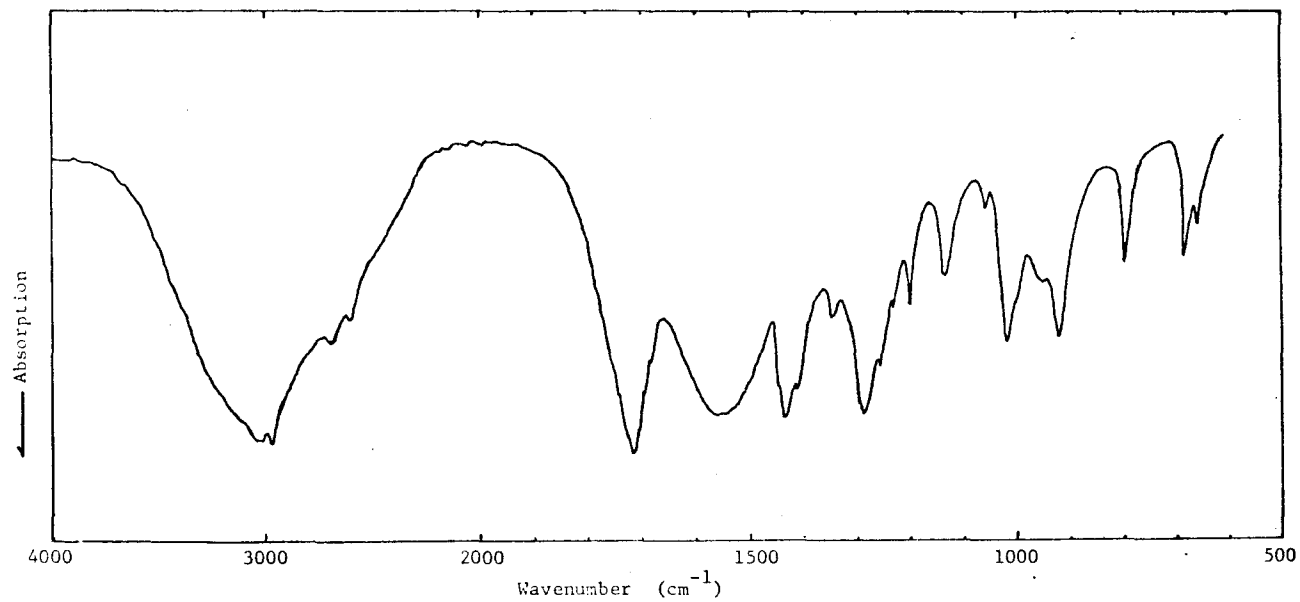


Fig. 6 The infrared spectrum of 3-carboxymethylthio-2,4-pentanedione

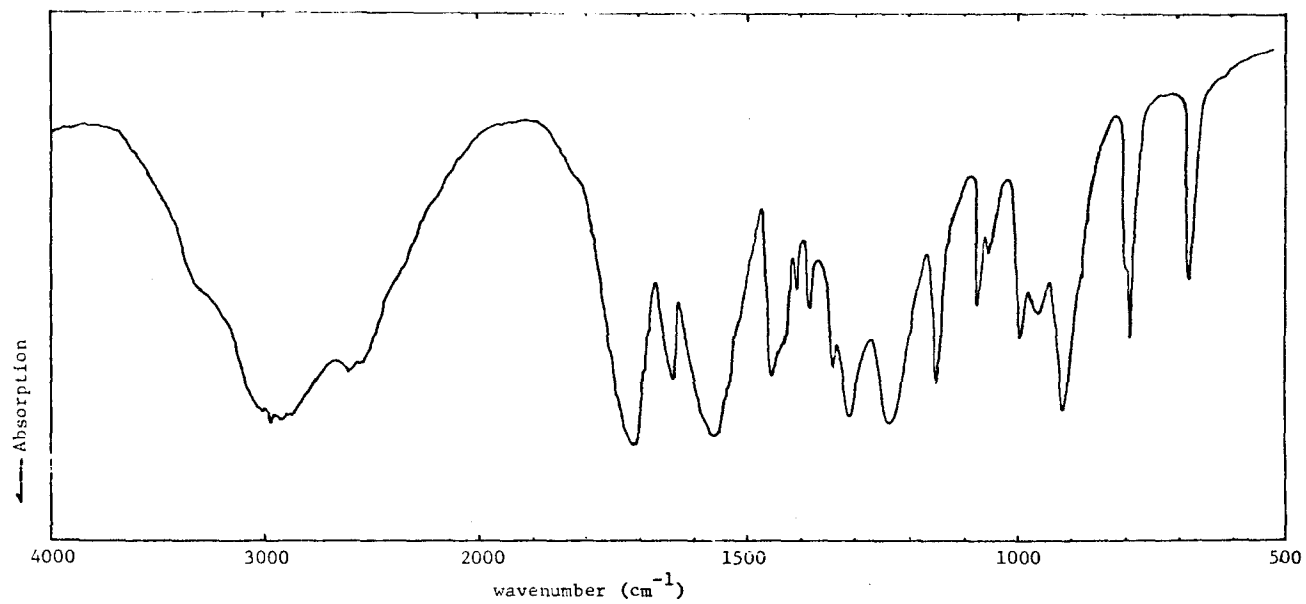
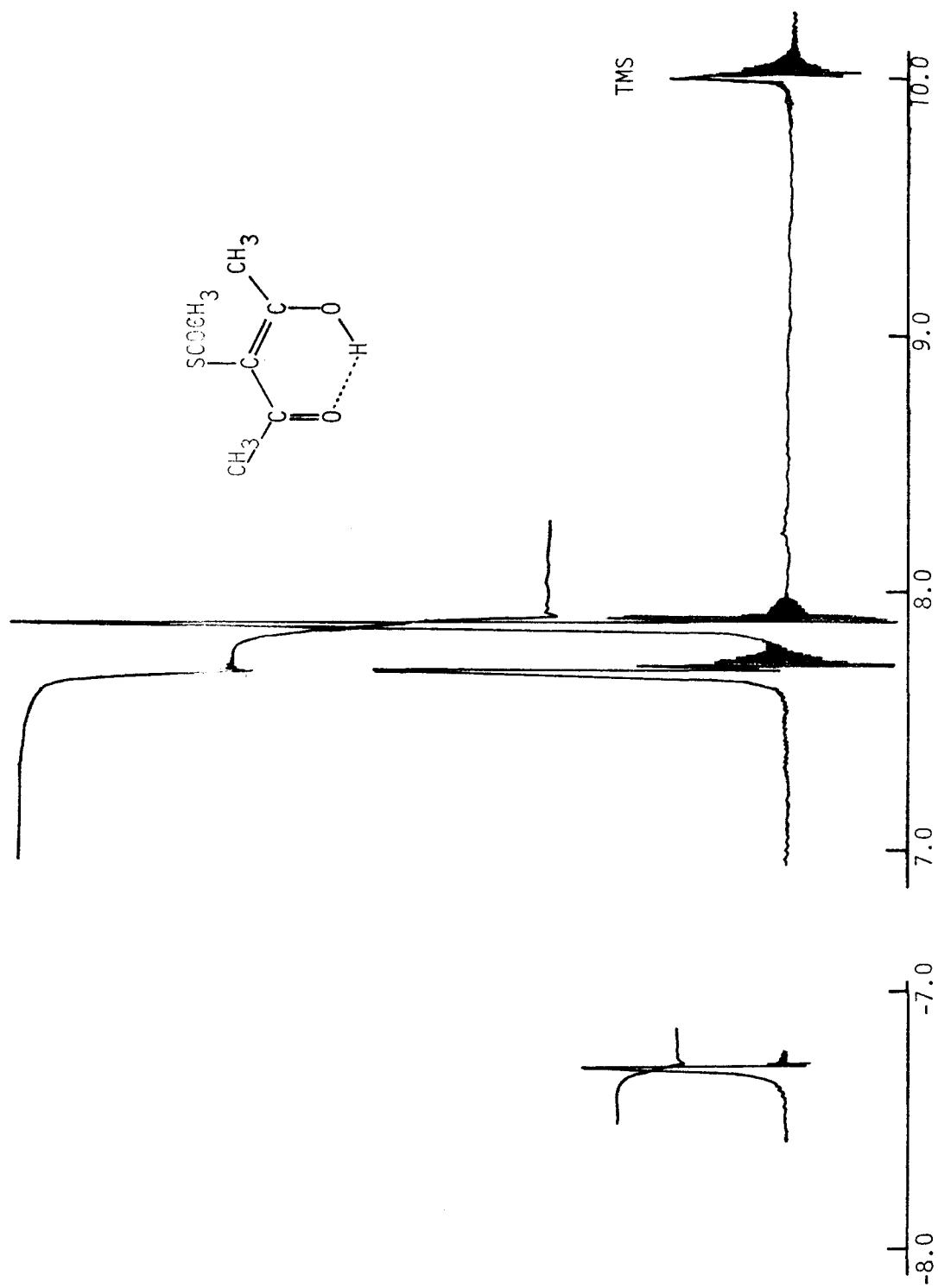


Fig. 7 The infrared of methyl α -carboxymethylthioacetate

Fig.8 Nmr spectrum of 3-acetylthio-2,4-pentanedione



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Chapter 5

The Reaction of Metal(III) Chelates of 3-Bromo-2,4-Pentanedione with Thiophenoles*¹

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*¹ Presented before at the Annual Meeting of the Chemical Society of Japan held at Tokyo, April, 1969.

5.1 Summary

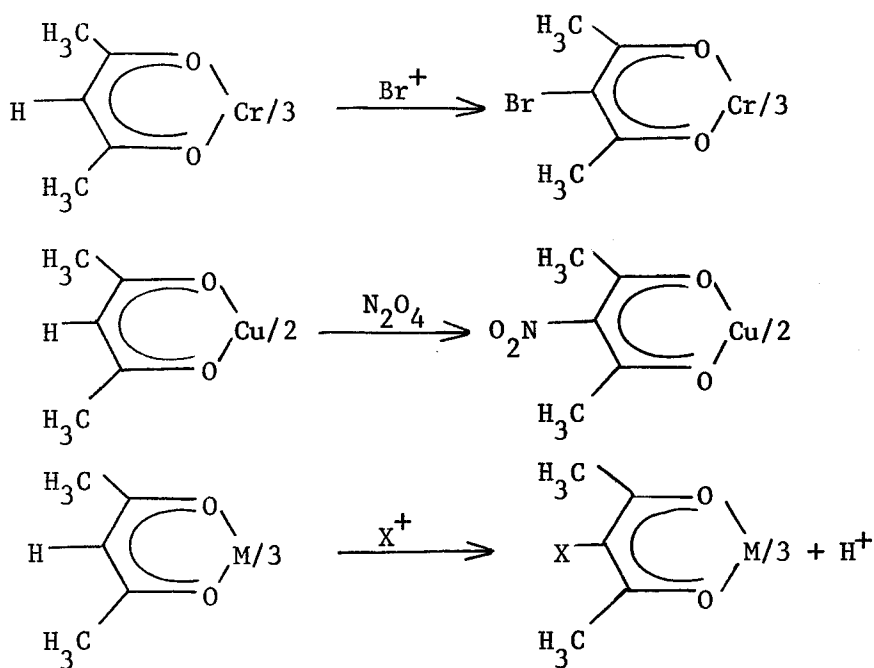
Although extensive works on electrophilic substitution reaction of acetylacetonates have been reported by many workers, successful cases of nucleophilic displacement at the central carbon of the chelate ring have never been found. We have succeeded in the first nucleophilic reaction of metal (III) acetylacetonate chelate ring by the reaction of tris-(3-bromo-2,4-pentanediono)-aluminum (III), -cobalt(III), and -chromium(III) with arylmercaptans, leading to yield tris-(3-arylthio-2,4-pentanediono)-metal (III) chelates. The proposed structures were confirmed by spectroscopic evidences and analyses.

The reaction in stronger proton acceptor such as acetone, methylalcohol, and diethylether was extremely depressed in comparison with the system in weaker proton acceptor such as benzene and methylenedichloride. The reaction behavior is qualitatively discussed in terms of the solvent effect, the substituent effect of nucleophiles and metals.

5.2 Introduction

It has been of great interest that trivalent metal chelate of acetylacetone undergo quasi-aromatic electrophilic substitution with a various reagents.¹ The first direct substitution was the bromination of chromium(III) acetylacetonate by the action of bromine in chloroform. Since Djoidjevic reported

nitration of copper (II) acetylacetonate,² it has invoked the attention of chemists to this field concerning with new aromatic system. Extensive works on electrophilic substitution have been reported by Collman and his co-workers.³

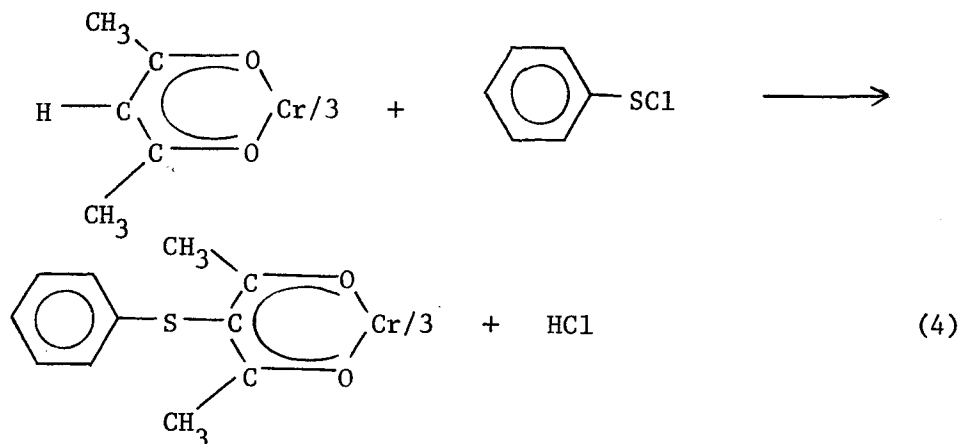


$\text{X}=\text{I}, \text{Br}, \text{Cl}, \text{SCN}, \text{SAr}, \text{SCl}, \text{NO}_2, \text{COCH}_3, \text{CHO}, \text{CH}_2\text{Cl}$

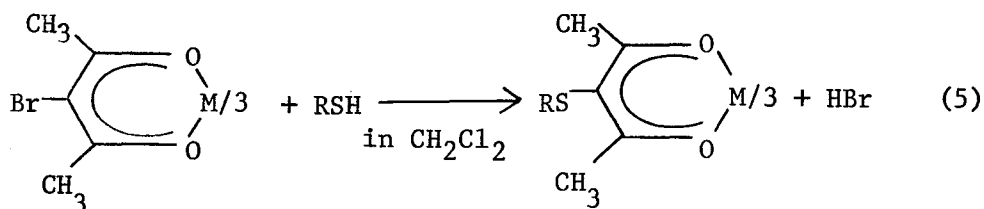
However, successful nucleophilic substitution have never been found anywhere. The treatment of tris-(3-bromo-2,4-pentanedione)-chromium(III) with azide, acetate, cyano, and iodo anion resulted in recovery of the starting material. In addition, the reaction of brominated chelate with sodium ethoxide in cold ethanol caused decomposition of metal chelate.⁴

Collman et al have reported that the treatment of tris-

(2,4-pentanediono-)-chromium(III) with sulfur nucleophile such as phenylsulfenyl chloride can afford tris-(3-phenylthio-2,4-pentanediono)-chromium(III) among his wide investigations.⁵



To the contrary, we have found an alternative nucleophilic pathway to prepare the above compound in milder condition using tris-(3-bromo-2,4-pentanediono)-metal (III) complexes and arylmercaptans in methylenedichloride at -5° - -20°. This is the first instance of the successful nucleophilic displacement to the central carbon atom of acetylacetonates.



M = Al(III), Co(III), Cr(III)

R = C₆H₅, p-CH₃C₆H₄, p-NO₂C₆H₄

5.3 Experimental

Starting materials; Acetylacetone was commercially available and distilled under nitrogen stream before use. Aluminum(III),⁶ cobalt(III),⁷ and chromium(III)⁸ acetylacetonates were prepared according to the authentic method. These chelates were halogenated by means of N-halosuccinimides followed by chromatography on silicagel. Commercial thiophenols were purified by distillation or recrystallization.

5.3.1 Tris-(3-phenylthio-2,4-pentanediono)-aluminum(III), (1a); Solution of tris-(3-bromo-2,4-pentanediono)-aluminum (1.0 g) in 60 ml. of methylenedichloride was kept at -20°C with dryice-acetone. To this solution was slowly added a solution of thiophenol in 10 ml. of methylenedichloride under stirring. After two hours, the solution was treated with aqueous sodium bicarbonate and washed with water three times. A white powder (0.26g.) was obtained from recrystallization from the mixture of water-ethanol.

5.3.2 Tris-(3-phenylthio-2,4-pentanediono)-cobalt(III)(2a); To a solution of tris-(3-bromo-2,4-pentanediono)-cobalt(III) (0.5g) in 40 ml. of methylenedichloride was dropwisely added a thiophenol (0.3g) in 10 ml of methylenedichloride at -20°C. After two hours at -20°C, 0.3g of pyridine was added to the solution at once. The reaction mixture was chromatographed on Florisil with benzene. A green solution was collected and

condensed to small portions under vacuum. Recrystallization from ethanol-water yielded a fine green crystals (0.3 g).

5.3.3 Tris-(3-phenylthio-2,4-pentanediono)-chromium(III), (3a); A solution of thiopenol (0.6 g) in 50 ml. of methylenechloride was slowly added to a solution of tris(3-bromo-2,4-pentanediono)-chromium(III) in 100 ml. of methylenedichloride at -5°C. The treatment similar to the method of (5.3.2) gave 0.52 g of reddish brown crystals. As an minor product, (2,4-pentanediono)-bis-(3-phenylthio-2,4-pentanediono)-chromium(III) was separated by thin layer chromatography, confirmed by infrared spectrum. Another metal(III) chelates were prepared according to the above described methods respectively.

Spectral measurements; Proton magnetic resonances of cobalt(III) and aluminium(III) chelates were measured on Japan Electron Laboratory, Model JNM C-60H in carbontetrachloride with TMS as an internal reference. Infrared spectra were recorded on Japan Spectroscopy Co., Model DS-402G grating spectrophotometer in KBr pellet. Hitachi Model EPS-3T spectrophotometer was used to study electronic spectra in methylenedichloride.

5.4 Results

Table 1 lists yields, physical properties and elementary analyses of products resulted from the reaction of brominated

acetylacetonates and arylmercaptans. Compound (3a) was obtainable in the yield of 32.7 % from the reaction of chromium(III) acetylacetonate with phenylsulfenylchloride.⁵ Alternative nucleophilic courses are possible to give corresponding compound (3a) by the reaction of tris-(3-bromo-2,4-pentanediono)-metal(III) with sulfur nucleophiles at low temperature. Eight complexes in Table 1 have never been reported anywhere except for (3a).

Nuclear magnetic resonance spectra

As is shown in Table 2, chemical shifts and ratio of integration for cobalt(III) and aluminum(III) complexes represent clear evidences to indicate the displacement of bromine with arylthio group. Furthermore, singlet signal of methyl group attached to the chelate ring does support that complexes are constructed with one species of ligands as is seen in Figure 1. Otherwise, chemical shift of methyl in the mixed ligand will be splitted into the two peaks because of their different magnetic field.^{10,11,12} The methyl protons of aluminum(III) complexes resonates at lower magnetic field by 0.18-0.24 ppm than those of cobalt(III) complexes in Figure 2. It is not clear the reason why difference due to the electronic field caused by central metal charge¹³ or the induced magnetic field of ring current of the chelates. Proton magnetic resonance of chromium(III) complexes are not measurable owing to paramagnetism of unpaired d-electron of chromium(III) ion. Hence the structure

of chromium(III) chelates were determined based on infrared and ultraviolet spectra.

Infrared spectra

Upon displacement of bromine with arylthio group, a few new absorptions appeared at 1494, 1481 and 1468 cm^{-1} assigned to skeletal stretching vibration of phenyl ring. In addition to those bands, another bands at 1086, 1073, 1059 and 1046 cm^{-1} are probably assigned to C-H in-plane bending vibration of phenyl ring and the C-S stretching vibration. The C-H out-of-plane bending of monosubstituted phenyl ring showed at 806 and 742 cm^{-1} . The latter one was disappeared on introduction of p-CH₃ and p-NO₂. Since new band at 708 cm^{-1} was not so sensitive to the para substituents, it is likely to be assigned to the stretching vibrational mode of S-C (central carbon atom of chelate).¹⁴ The chelates substituted with p-nitrophenylthio group revealed asymmetric stretching vibration of NO₂ at 1510 cm^{-1} and two absorptions at around 850 cm^{-1} which are possibly assigned to $\pi(\text{C-H})$ and $\nu(\text{C-N})$. p-Methyl phenylthio group would be characterized by the new absorption at 755 cm^{-1} due to the rocking vibration of methyl group. Infrared spectra of chromium(III) chelates in the region from 1800-400 cm^{-1} are demonstrated in Figure 2.

Ultraviolet spectra

The ultraviolet spectra and characteristic infrared spectra are listed in Table 3. Non substituted chelates exhibit strong absorption at 288, 258 and 336m μ for aluminum(III), cobalt(III) and chromium(III) chelate respectively.¹⁵ Similar strong absorption due to chelate ring is observed for each arylthio substituted chelate. As is seen in Table 3, another strong absorption at 252(1a), 254(1b) and 340(1c) are assigned to the local excitation band $\pi-\pi^*$ transition of para substituted phenyl ring in aluminum(III) chelates. Unfortunately, accidental overlapping of absorption related to the chelate ring and the arylthio group occurred in the cases of (2a), (2b) and (3c) with increases of the strength of absorption.

Reactivity of halogens

In order to elucidate the reaction mechanism, the reaction of tris-(3-chloro-2,4-pentanediono)-cobalt(III) with thiophenol was carried out under the same condition as the case of (6.3.2). The starting material was recovered from the resultant reaction mixture. Even though temperature was raised up to room temperature, trace of (2a) was detected by means of thin layer chromatography. On the other hand, treatment of tris-(3-iodo-2,4-pentanediono)cobalt(III) with thiophenol yielded (2a) to the same extent as the brominated chelates. Consequently, reactivity of halogens are shown in the following order $I, Br > Cl$. The bond

C-X breaking step seems to be significant kinetically.

Effects of oxygen and light

As is well known facts, mercaptans can undergo radical reaction in the presence of oxygen or under irradiation of light. To assure the these effects, the reaction of cobalt (III) chelates with thiophenol was carried out in the dark place under nitrogen stream. As a matter of fact, the significant acceleration or depression of the reaction was not observed within experimental error. Radical reaction scheme is probably less possible.

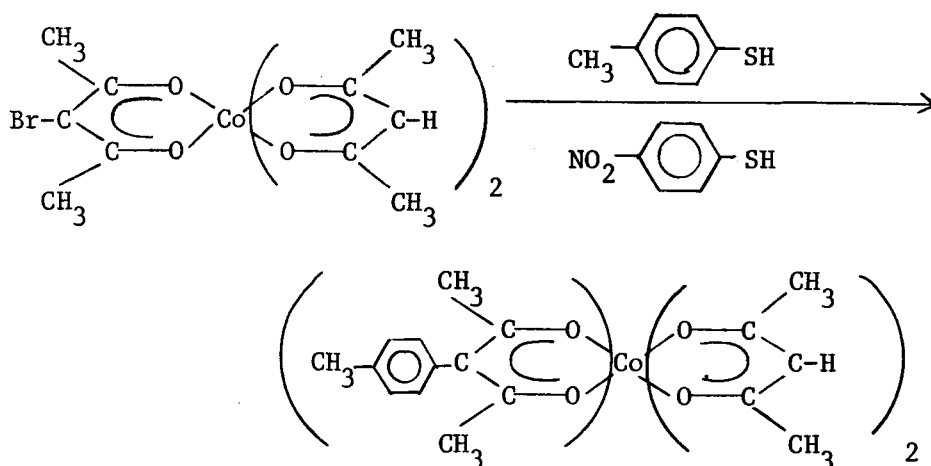
Effect of solvents

Metal(III) acetylacetonates used to be soluble in usual organic solvents. A solvent effect on the reaction involving metal chelates has never been taken into consideration. Various solvents such as acetone, diethylether, methylalcohol and dimethylsulfoxide were used in order to study the effect of solvent on the reaction. Reaction proceeds effectively in benzene as well as in methylenechloride. To the contrary, it is worthy of notice that the reaction in stronger proton acceptor such as acetone, methanol, ether and dimethylsulfoxide was entirely inhibited. Therefore, it must be mentioned that the effect of solvent is considerably larger than in the electrophilic displacement reaction. An addition of amine such as pyridine and piperidine to accelerate nucleophilic displacement resulted in a failure

to initiate the reaction under the same condition as (5.3.2.).

Effect of substituents in arylthio group

To avoid difficulties to separate the mixed ligands chelate resulted from competitive reaction of different nucleophiles to a tri-halogenated metal(III) chelate, mono brominated chelate, (3-bromo-2,4-pentanediono)-bis-(2,4-pentanediono)-cobalt(III) was used to investigate the effect of substituents in arylthio group on the reaction. A competitive nucleophilic displacement of p-nitro and p-methyl thiophenol to mono brominated cobalt (III) chelate showed the presence of the exclusive product substituted with p-methylphenylthio group which was clearly proved by NMR spectra of the product. It is, therefore, concluded that the nucleophilicity of sulfur is enhanced by the electron donating substituent and lowered by the electron attracting one. This trend is surprisingly similar to the nucleophilic substitution of thiophenols toward 2,4-dinitrochlorobenzene.¹⁶

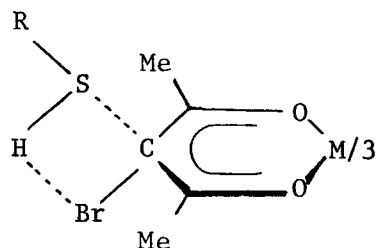


5.5 Discussion

Despite of extensive works on the electrophilic reaction, there have never been reported quantitative reaction kinetics and mechanisms from the standpoint of the quasi aromatic ring of metal chelates except for the mechanisms of bromination by Kluiber.¹⁷ It was suggested that the consequent of the electron shift from chelate ring to the metal will reduce the tendency towards electrophilic substitution. On the contrary to expectation, only electrophilic substitutions have been developed and successful as has been reported.

An insignificant effect of oxygen and light seems to exclude radical mechanism to explain the reaction scheme in this system. It is reasonably assumed from the effect of solvent that weakly polarized sulfur nucleophiles might participate in the center of reaction rather than completely ionized species.¹⁸ The sequence of reactivity of leaving halogens would be explained in terms of polarizability of halogens rather than their electronegativities. Moreover, the great polarizability of sulfur atom enables sulfur nucleophile to form the C-S bond easily. Thus both polarizability of attacking sulfur nucleophile and leaving halogen seems to play kinetically important role on the transition state. The presence of strong proton acceptor may break the plausible four centered intermediate to form favorable intermolecular hydrogen bond of $\text{-SH---O} <$

and $\text{--SH--N} \leftarrow$.



It is of particular interest to discuss about the effect of metals on the reaction. In case of chromium(III) complexes, reaction temperature was raised up to -5°C to initiate reaction. Therefore, the reactivity of chromium(III) complex is lower than that of cobalt(III) complex judging from the severity of condition. On the other hand, in electrophilic substitution such as acylation, chromium(III) chelates were found to be more reactive than that of cobalt(III).

It can be considered that charge transfer from metal to ligand or ligand to metal may be possible through d-orbitals of metal to interpret the electronic effect of metal. However, it is rather difficult to attribute the electronic effect to d-electron of metal generally, because aluminum(III) chelate showed potential reactivity to sulfur nucleophile under the same condition as cobalt(III) and chromium(III) complexes, even though aluminum possesses no available d-electrons.

In nucleophilic displacement, it should be noticed that there are two kinds of reaction sites, that is, the central

carbon atom and metal. An attack of nucleophile to metal possibly leads exchange of ligands followed by the decomposition of the chelate ring at higher temperature. Especially strongly ionized nucleophiles may have the trend to decomposition. This fact has been observed in the reaction of bis-(3-chloro-2,4-pentanediono)-copper(II) chelate with thiophenol resulted in ready decomposition to give copper sulfide.

Table 1 Physical properties of metal (III) chelates

Metal	R	Yield (%) [*]	m.p. (°C)	Anal (%)			
				Cal.		Found	
				H	C	H	C
Al(III)	C ₆ H ₅	23	65 - 67	5.13	61.11	5.63	59.08
Al(III)	p-CH ₃ C ₆ H ₄	53.5	162-164	5.69	62.60	5.75	63.78
Al(III)	p-NO ₂ C ₆ H ₄	18.6	135-137	3.86	50.58	4.18	51.20
Co(III)	C ₆ H ₅	45.3	104-106	4.89	58.24	5.30	58.52
Co(III)	p-CH ₃ C ₆ H ₄	44.8	170-171	5.44	59.83	5.65	59.87
Co(III) ^{**}	p-NO ₂ C ₆ H ₄	43.5	163-165	3.61	47.38	3.87	47.48
Cr(III)	C ₆ H ₅	90	105-107	4.94	58.84	5.16	59.07
Cr(III)	p-CH ₃ C ₆ H ₄	68.6	100-102	5.49	60.41	5.57	58.21
Cr(III)	p-NO ₂ C ₆ H ₄	88.6	148-150	3.74	49.01	4.00	49.68

* Based on chelate

** The sample was found to contain 0.36 mole % of CH₂Cl₂ as impurity determined from the n.m.r. spectrum.

Table 2 The NMR spectra of Al(III) and Co(III) chelates*

τ (ppm)				
Metal	R	CH_3	R	
Al(III)	C_6H_5	7.63(s, 18H)	2.90-3.05(m, 15H)	
Al(III)	$\text{p-CH}_3\text{C}_6\text{H}_4$	7.64(s, 18H)	3.05(s, 12H)	7.76(s, 9H)
Al(III)	$\text{p-NO}_2\text{C}_6\text{H}_4$	7.63(s, 18H)	2.01(d, 6H)	2.82(d, 6H)
Co(III)	C_6H_5	7.46(s, 18H)	2.92-3.05(m, 15H)	
Co(III)	$\text{p-CH}_3\text{C}_6\text{H}_4$	7.50(s, 18H)	3.06(s, 12H)	7.77(s, 9H)
Co(III)	$\text{p-NO}_2\text{C}_6\text{H}_4$	7.40(s, 18H)	1.90(d, 6H)	2.75(d, 6H)

* Measured in CCl_4 using TMS as an internal standard s, d, and m denote singlet, doublet and multiplet respectively.

Table 3 The IR and UV spectra of metal (III) chelates

Metal	R	IR (in KBr, cm^{-1})*			UV (in CH_2Cl_2 , $\text{m}\mu$)	
		$\nu(\text{C}=\text{C})$	$\pi(\text{CH})$	$\nu(\text{C}-\text{N})$	λ_{max}	(log ϵ)
Al(III)	C_6H_5	1480	805		252(4.53)	291(4.43)
Al(III)	$\text{p-CH}_3\text{C}_6\text{H}_4$	1495	808		254(4.56)	290(4.43)
Al(III)	$\text{p-NO}_2\text{C}_6\text{H}_4$	1478	842	853	340(4.56)	292(4.54)
Co(III)	C_6H_5	1482	805		253(4.77)	
Co(III)	$\text{p-CH}_3\text{C}_6\text{H}_4$	1495	807		255(4.83)	
Co(III)	$\text{p-NO}_2\text{C}_6\text{H}_4$	1477	842	852	341(4.69)	255(4.53)
Cr(III)	C_6H_5	1481	806		252(4.51)	335(3.94)
Cr(III)	$\text{p-CH}_3\text{C}_6\text{H}_4$	1495	806		254(4.65)	334(4.03)
Cr(III)	$\text{p-NO}_2\text{C}_6\text{H}_4$	1477	841	852	340(4.72)	

* Showed only characteristic bands and calibrated by polystyrene film.

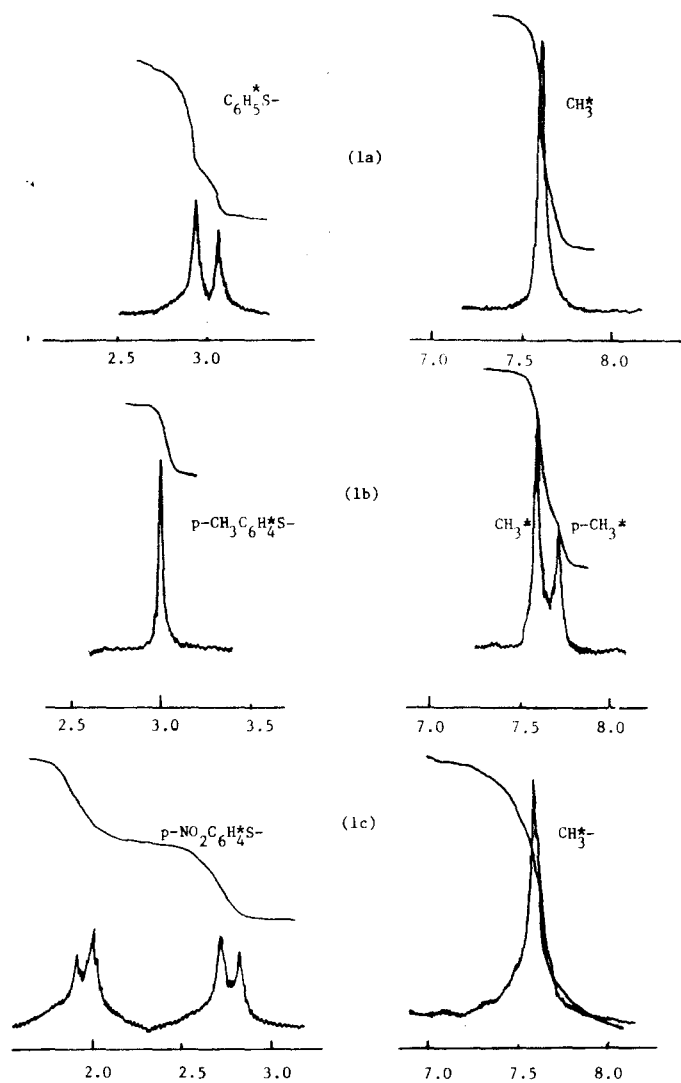


Figure 1 The NMR spectra of tris-(3-arylthio-2,4-pentanedione) aluminum(III)

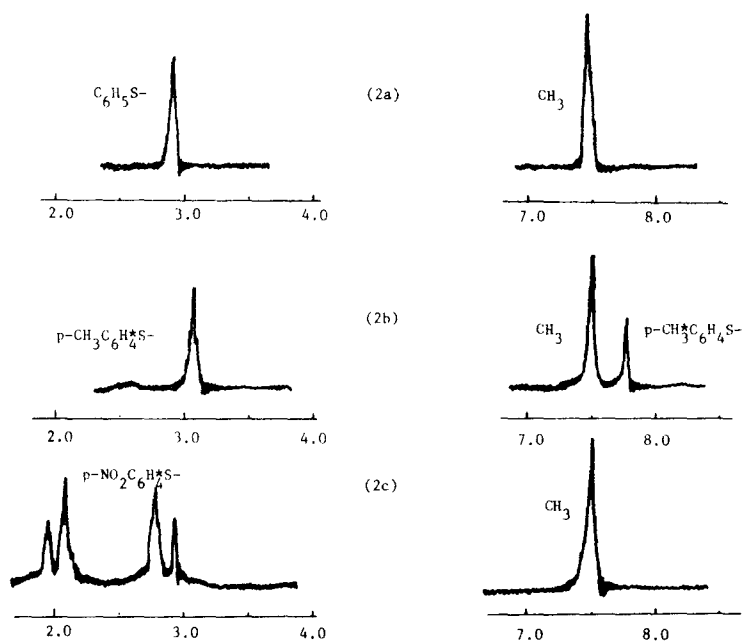


Figure 2 The NMR spectra of tris-(3-arylthio-2,4-pentanedione)
cobalt (III)

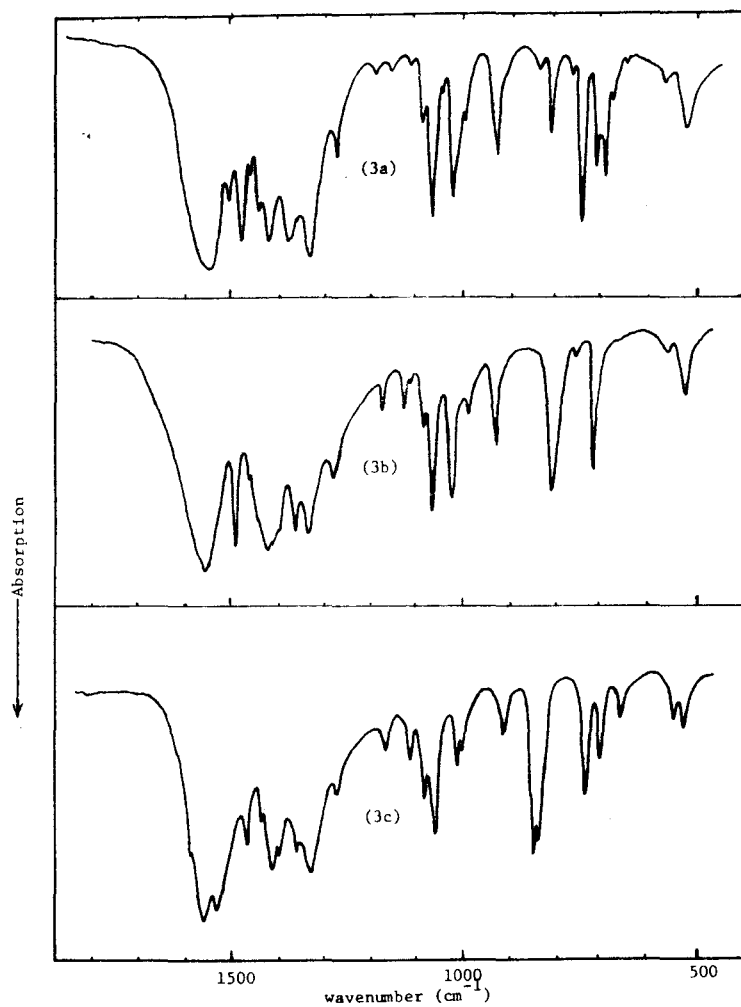


Figure 3 The IR spectra of tris-(3-arylthio-2,4-pentanediono) chromium (III)

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Chapter 6

Cyclopropyl Conjugation with the Chelate Ring of β -dicarbonyls^{*1}

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*1 Presented before at the Annual Meeting of the Chemical Society of Japan at Tokyo, April 1969.

6.1 Summary

π -Conjugative effect of cyclopropyl ring on the chelate ring of β -diketones at the both ground and excited state has been studied by means of spectroscopic methods. The changes in spectra have been compared on the substitution of isopropyl group with cyclopropyl ring. Proton magnetic resonance and infrared spectra indicate that there is appreciable conjugative effect at the ground state. The bathochromic shift of $\pi-\pi^*$ transition band of the chelate ring suggests more stabilization of the excited state rather than the ground state. Conformational preference of cyclopropyl ring in the chelate ring of β -diketones become more important at the excited state. Cyclopropyl conjugation in metal chelate of β -diketone appears to be considerably small in comparison with free ligand.

6.2 Introduction

Problems of π -conjugative interaction of cyclopropyl ring with adjacent unsaturated bond have been a great deals of chemist.¹ It has been of particular interest that conformational preference of cyclopropyl reflects on the overlapping of p-orbital of adjacent double bond.^{2,3} Even though so many works have been reported, a large number of them is concerned with electronic spectra with less care of the ground state.⁴⁻⁷ The cyclopropyl conjugation at the ground state have recently

been investigated by the techniques of proton magnetic resonance,⁸⁻¹⁰ infrared,^{11,12} electron diffraction,^{13,14} and solvolysis reaction.¹⁵

The system of enolic structure of β -diketones present the proper example in order to study rather weak conjugative effect of cyclopropane ring, since π -electron system associated with intramolecular hydrogen bond enable to give information about both ground and excited state. Several new cyclopropyl substituted β -diketones have been reported in the present paper.

6.3 Experimental

1-Cyclopropyl-3-isopropyl-1,3-propanedione (II); Essential procedure were followed according to the method to prepare asymmetric β -diketone reported by Linn and Hauser.¹⁶

A solution of 8.04 g (0.096 mole) of cyclopropylmethylketone in 100 ml of ethylether was slowly added to suspension of 7.0 g (0.18 mole) of finely pulverized sodium amide under vigorous stirring for 30 min. To reaction mixture was dropwisely added 32.0 g (0.27 mole) of ethyl iso-butyrate followed by further stirring for 3 hr at room temperature. A gelatinous mixture was poured into ice-water and neutralized by 6N-HCl. β -Diketone was separated by treatment of aqueous copper acetate in the form of bis-(1-cyclopropyl-3-isopropyl-1,3-propanediono)

-copper(II). Copper chelate recrystallized from chloroform was hydrolyzed by 6N-HCl. β -Diketone was recovered by extraction with ether. Extract was washed with water and dried over anhydrous sodium sulfate. Distillation at reduced pressure afforded 6.5 g of a colorless liquid, 54.0–55.5°C/6mm, 44% yield based on ketone.

1,3-dicyclopropyl-1,3-propanedione (III), 1-cyclopropyl-3-(2-thenoyl-1,3-propandione (IX), 1-cyclopropyl-3-(2-furyl-1,3-propanedione (VII), and 1-cyclopropyl-3-trifloromethyl-1,3-propnedione (XI) were prepared using corresponding ketone and ester. In case of (XI), ether extract was refluxed with P_2O_5 for 5 hr. Its elementary analysis was doubtful because of the action of fluorine, however structural identification was supported by nmr spectrum. Colorless liquid was separated by distillation.

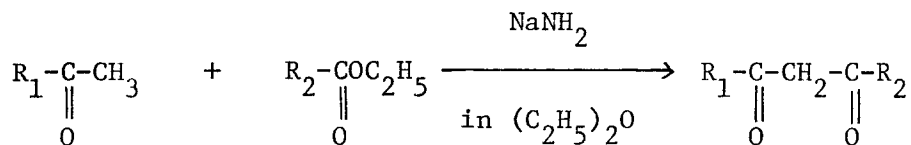
Spectral Measurements

Spectrophotometers used in this work were stated in the previous chapter. Infrared spectra were measured in carbon tetrachloride. Measurement of ultraviolet and visible spectra were carried out in n-hexane for β -diketones and in methylene-chloride for copper chelates respectively

6.4 Results and Discussion

Table 1 lists yield, physical properties and elementary analysis of newly synthetized cyclopropyl substituted β -diketone.

The synthetic pathway of 1,3-diketones



R_1 = cyclopropyl, isopropyl

R_2 = cyclopropyl, isopropyl, phenyl, 2-furyl, 2-thienoyl,
trifluoromethyl

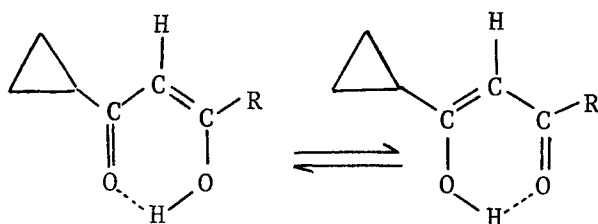
¹⁷
Cannon and Whidden have already synthesized cyclopropyl substituted β -diketones such as 1-cyclopropyl-1,3-butanedione and 1-cyclopropyl-3-phenyl-1,3-propanedione, however they have never mentioned about available spectroscopic data. Their nmr spectra in carbon tetrachloride are shown in Figure 1 - Figure 4. No cleavage of cyclopropane ring has been proved by the spectroscopic evidences and the elementary analyses. As has been explained by Hammond et al,¹⁸ substitution of bulky groups at 1- and 3-positions increases the percentage of enol tautomer owing to repulsive interaction between two substituents. Similar high enolization has been proved by the nmr spectra. The enolization of cyclopropyl substituted β -diketones are not different from corresponding isopropyl substituted β -diketone. All of them showed more than 90 % of enol structure estimated from the ratio of integration of the $-\text{CH}_2-$ proton of keto form and the $-\text{CH=}$ of enol form.

Chemical shifts of β -diketones are summarized in Table 2. Two chemical shifts, $-\text{CH}=\text{}$ and $\text{O}-\text{H}\cdots\text{O}$, characteristic of the chelate ring were noticed to evaluate the changes in π -conjugative system and the strength of intramolecular hydrogen bond. The proton chemical shifts of the $-\text{CH}=\text{}$ resonate slightly at lower magnetic field compared with corresponding iso-propyl substituted β -diketones. Similar trend have been observed in cyclopropyl substituted olefinic esters, where the $-\text{CH}=\text{}$ proton of trans conformer appeared at lower magnetic field than cis conformer.¹⁹ However, it is rather hard to show whether a cyclopropyl ring exist in s-trans or s-cis to the $\text{C}=\text{C}$ bond of the chelate ring.

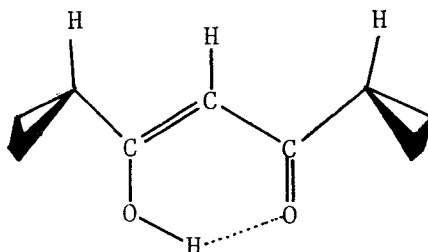
As has been reported by Jarret et al,²⁰ the enolic proton resonates at quite lower magnetic field. The position of chemical represents a measure of the strength of hydrogen bond in accord with a shift of carbonyl stretching vibration in infrared spectra.²¹ Substitution of iso-propyl with cyclopropyl indicates an appreciable down field shift for 3-isopropyl, 3-thenoyl and 3-trifluoro series. On the other hand, slight up field shift are observed in 3-phenyl and 3-fruyl substituted ones. As is seen in Table 3, the $\text{C}=\text{O}$ stretching shifted appreciably to lower frequency region for former group and for the latter case, the shift was only few wave numbers on substitution with cyclopropyl group. Strictly speaking, the indication

by the C=O stretching is rather vague because of its superimposition with the C=C stretching.²²

There exist possible interconvertible enol isomers (A) and (B) for asymmetric β -diketones, even though its potential barrier between two isomers seems to be very small. In nmr spectrum, it is impossible to distinguish whether (A) or (B) is predominant structure at equilibrium.²⁰ Averaged chemical shifts of (A) and (B) used to be measured owing to rapid interconversion. If one enol structure is more stable than the other, the nmr spectrum belonged to the former would be reflected on the averaged spectrum. According to this consideration, it is explainable that cyclopropyl substitution exhibit different effect on hydrogen bonding. Electron supplying cyclopropyl adjacent to carbonyl in A form enhances the electron density on the oxygen of carbonyl increasing the strength of hydrogen bond whereas it in B form close to enol increases the electron density on the oxygen of enol resulted in weaker hydrogen bond due to less proton releasing.



Conformational studies on cyclopropyl carbonyls by electron diffraction¹⁴ have suggested that s-cis rotational isomer is preferential rather than s-trans conformer at the ground state. This is evidently supported by vibrational spectrum of cyclopropanecarboxylic acid chloride.¹² It has been proposed that s-trans rotational isomer is the lower energy conformer on the basis of analysis of nmr spectra of vinylcyclopropane. These results lead us to suppose that one of two cyclopropyl ring of 1,3-dicyclopropyl-1,3-propanedione (III) is placed in s-cis configuration to the carbonyl and the other one is s-trans to perform maximum overlap with p-orbitals of the chelate ring recognized from Walsh's model.²³











The electronic spectra of β -diketones are given in Table 3.

Cyclopropyl substitution cause the bathochromic shift of the $\pi-\pi^*$ transition of the chelate ring which are smaller than that of olefinic esters. Among them, β -diketones containing heterocyclic group and strong electronegative group show somewhat larger shift than those of iso-propyl and aryl substituted

β -diketones. Charge separation of former at the excited state become more significant on substitution with cyclopropyl compared with the latter cases. It is concluded that cyclopropyl ring seems to interact more effectively with π -electron system of the chelate ring at the electronically excited state than the ground state, since the change in electronic spectra are related to the energy difference between the ground and excited states. Cyclopropyl conjugation with metal chelate interest us for its quasi-aromatic ring in comparison with phenylcyclopropane.^{4,8} However, substitution with cyclopropyl has never shown such appreciable changes at the both ground and excited states as are seen in metal free chelate. Table 4 and 5 list ultra-violet and visible spectra of metal chelates respectively. Although band (I) at around 250 m μ assigned to σ (ligand) \rightarrow d_{xy} (metal) transition²⁴ reveals very small shift to lower wave length, it is rather difficult to interpret the electronic effect of cyclopropyl group on the bonding of metal and ligand without precise molecular orbital calculation. Band(II) appeared at 290-340 m μ due to $\pi-\pi^*$ transition²⁵ of chelate ring does not show significant changes which represent less interaction between cyclopropyl group and the chelate ring as is seen in phenylcyclopropane. Broad absorptions in the visible region seem to be less accurate to discuss, because the positions of maximum absorption are hard to be determined. The chelated $\underline{C}\cdots O$ stretching vibration appeared at 1580 cm⁻¹ was not

sensitive to the substitution with cyclopropyl group. Therefore, it seems to suggest that effect of cyclopropyl group on the metal chelate is very little at the ground state.

Table 1 The Physical Properties of 1,3-Diketones

R ₁	R ₂	Yield(%) [*]	bp(°C/mm)	Calcd, %			Found, %		
				C	H	S	C	H	S
		49.4	86-88/8	7.95	71.02		8.15	71.75	
		44.0	55-56/6	9.15	70.12		9.43	70.32	
		32.0	91-92/6	5.91	67.98		5.96	67.98	
		52.0	142-144/4	5.15	61.85	16.49	5.20	62.42	16.53

* base on ketone

Table 2 The nmr spectra of β -diketones





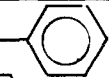
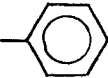

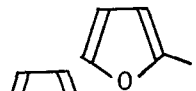
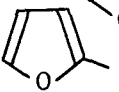

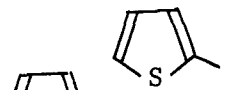
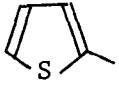


	R_1	R_2	τ_{CH}	τ_{OH}	R_1 $-\text{CH}(\text{CH}_3)_2$ or 	R_2
(I)	$-\text{CH}(\text{CH}_3)_2$,	$-\text{CH}(\text{CH}_3)_2$	4.56	-5.34	7.56(2H, m), 8.84(8H, d)	
(II)	$-\text{CH}(\text{CH}_3)_2$,		4.49	-5.66	7.62(1H, m), 8.85(6H, d)	8.40(1H, m), 9.10(4H, m)
(III)			4.35	-5.76	8.45(1H, m), 9.02(8H, m)	
(IV)		$-\text{CH}(\text{CH}_3)_2$	3.93	-6.32	2.20(2H, m), 2.60(3H, m)	7.44(1H, m), 8.80(6H, d)
(V)			3.84	-6.27	2.25(2H, m), 2.65(3H, m)	8.16(1H, m), 8.94(4H, m)
(VI)		$-\text{CH}(\text{CH}_3)_2$	4.00	-5.37	3.50(1H, m), 2.94(1H, d) 2.53(1H, d)	8.80(6H, d), 7.47(1H, m)
(VII)			3.93	-5.29	3.50(1H, m), 3.03(1H, d) 2.54(1H, d)	8.29(1H, m), 8.90(4H, m)
(VIII)		$-\text{CH}(\text{CH}_3)_2$	4.10	-5.77	2.95(1H, m), 2.45(2H, m)	7.50(1H, m), 8.80(6H, d)
(IX)			3.96	-6.00	2.98(1H, m), 2.50(2H, m)	8.34(1H, m), 8.92(4H, m)
(X)	CF_3	$-\text{CH}(\text{CH}_3)_2$	4.12	-3.53		7.45(1H, m), 8.78(6H, d)
(XI)	CF_3		3.98	-4.69		8.22(1H, m), 8.80(4H, m)

Table 3 The ultraviolet spectra of copper(II)
chelate of β -diketones


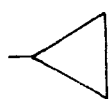


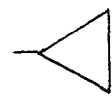

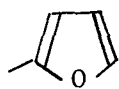
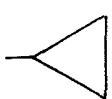
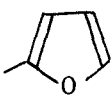
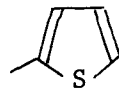
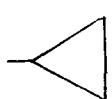
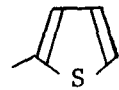
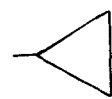
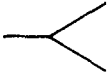

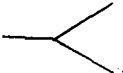



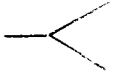
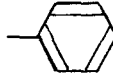

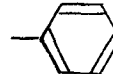
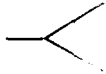
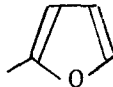
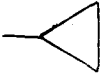
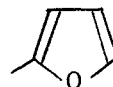
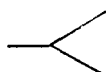
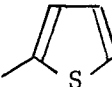

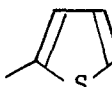
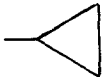
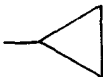
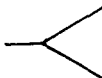
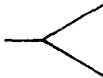
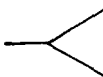
R_1	R_2	$\lambda_{\max}(\log \epsilon)$ ($m\mu$)	$\nu(\text{C=O}) \text{ cm}^{-1}$
$-\text{CH}(\text{CH}_3)_2$	$-\text{CH}(\text{CH}_3)_2$	273.5 (4.13)	1613
$-\text{CH}(\text{CH}_3)_2$		277.0 (4.12)	1610
		284.0 (4.11)	1584
$-\text{CH}(\text{CH}_3)_2$		307.0 (4.42)	1573
		315.0 (4.23)	1571
$-\text{CH}(\text{CH}_3)_2$		310.0 (4.36)	1610
		323.5 (4.43)	1607
$-\text{CH}(\text{CH}_3)_2$		318.0 (4.26)	1605
		331.0 (4.25)	1582
$-\text{CH}(\text{CH}_3)_2$	$-\text{CF}_3$	282.5 (3.84)	1612
	$-\text{CF}_3$	295.5 (3.85)	1598

Table 4 UV spectra of copper (II) chelates of 1,3-diketones*

		(I)	(II)
R_1	R_2	λ_{\max} (log ϵ)	
		251.1 (4.08)	299.9 (4.36)
		249.1 (4.29)	298.5 (4.49)
		248.2 (4.36)	300.0 (4.59)
		261.0 (4.45)	325.4 (4.57)
		258.5 (4.37)	327.4 (4.55)
			336.2 (4.59)
			336.5 (4.76)
		266.5 (4.29)	340.5 (4.57)
		265.8 (4.22)	341.0 (4.54)

* measured in methylenedichloride

Table 5 Visible Spectra of Copper (II) Chelate*

R ₁	R ₂	λ_{max} (log ϵ) m μ	
		(III)	(IV)
-CH(CH ₃) ₂	-CH(CH ₃) ₂	555 (1.606)	663 (1.696)
		554 (1.626)	664 (1.698)
C ₆ H ₅ -	-CH(CH ₃) ₂	550 (1.636)	660 (1.680)
C ₆ H ₅ -		550 (1.542)	658 (1.628)
2-C ₄ H ₉ O-	-CH(CH ₃) ₂	545 (1.540)	655 (1.660)
2-C ₄ H ₉ O-		552 (1.552)	658 (1.618)
2-C ₄ H ₉ S-	-CH(CH ₃) ₂	550 (1.765)	656 (1.716)
2-C ₄ H ₉ S-		553 (1.700)	658 (1.700)

* measured in methylenedichloride

Fig. 1 The nmr spectrum of 1,3-dicyclopentyl-1,3-propanedione

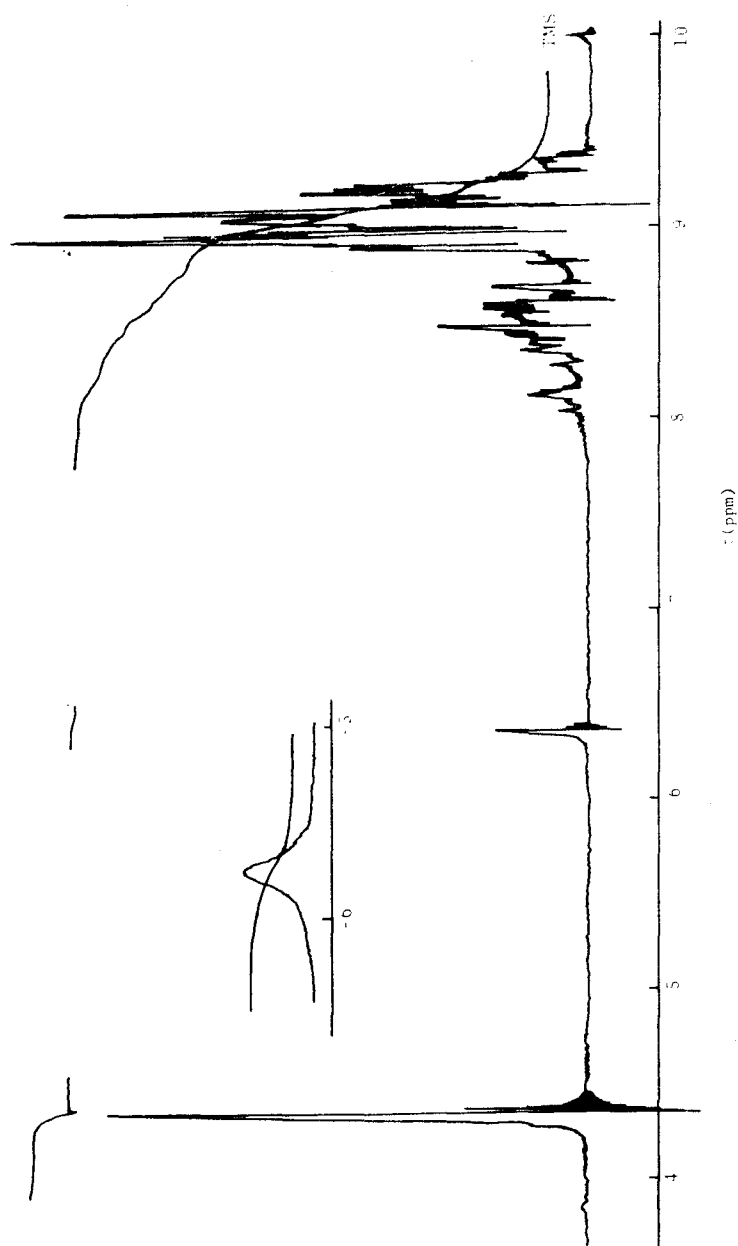


Fig. 2 The nmr spectrum of 1-cyclopropyl-3-trifluoromethyl-1,3-propanedione

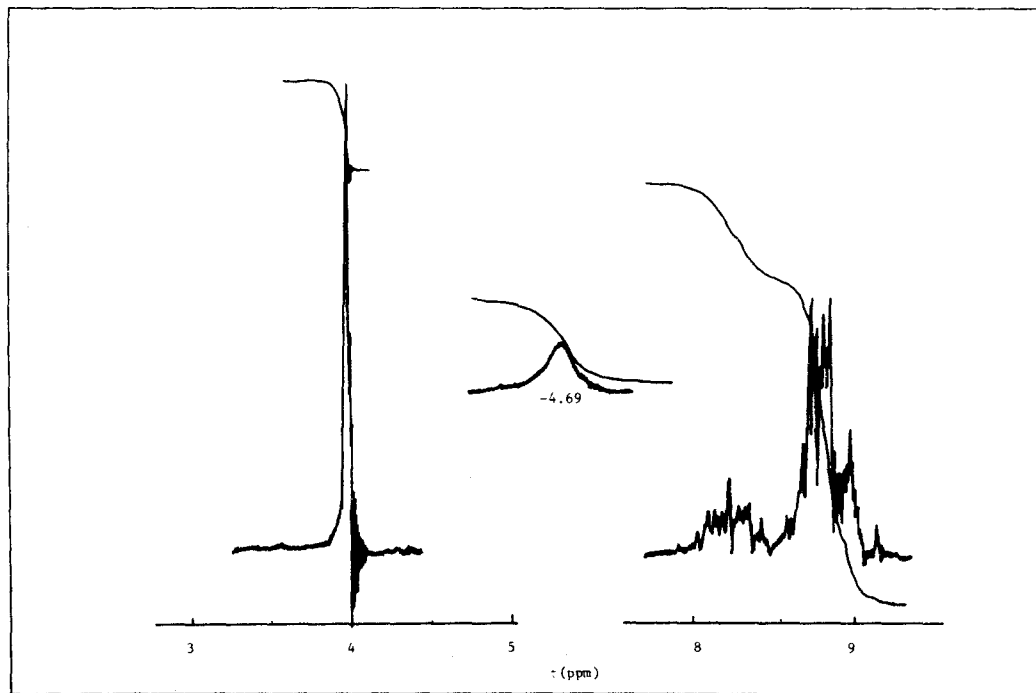


Fig. 3 The nmr spectrum of 1-cyclopropyl-(2-furyl)-1,3-propanedione

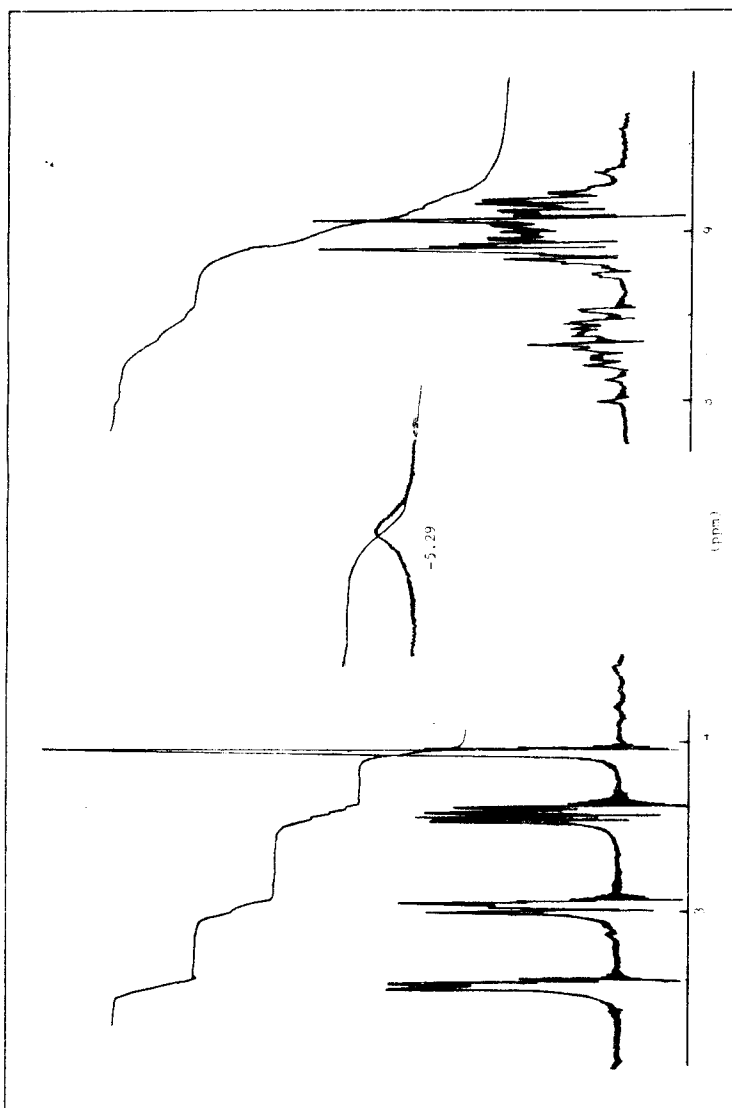
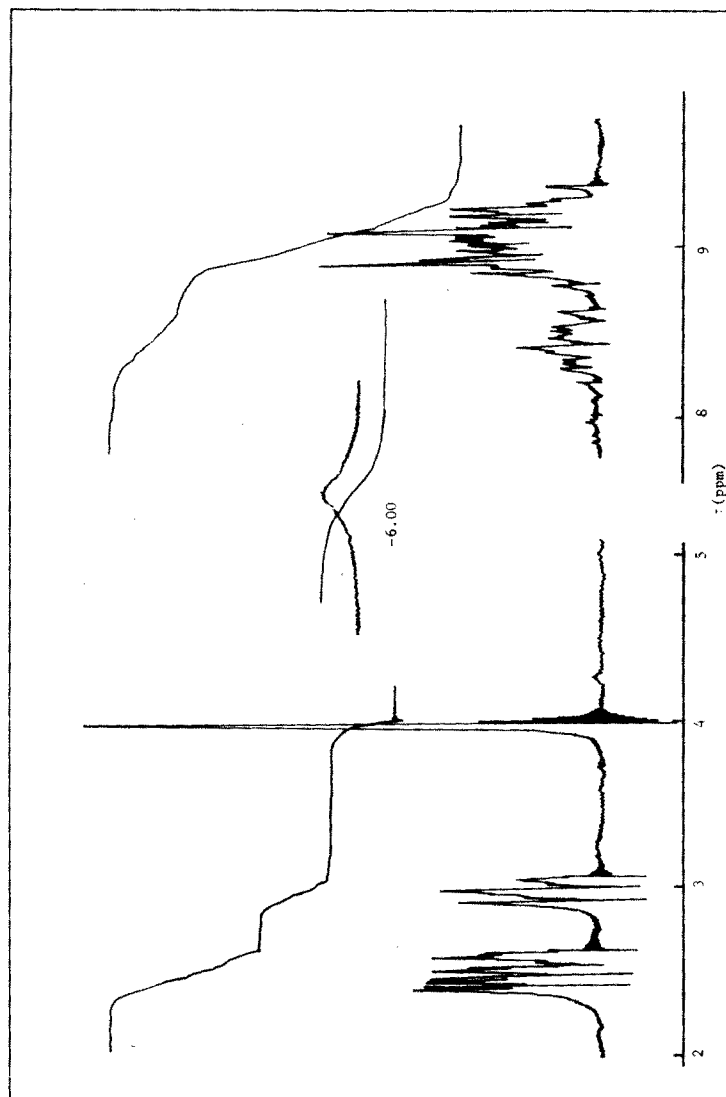


Fig. 4 The nmr spectrum of 1-cyclopropyl-(2-thenoyl)-1,3-propanedione



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Chapter 7

Molecular Orbital Calculations in Hückel and SCF Approximation; The Enolate Ion^{*1}

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7.2 Introduction	144
7.3 The procedure of Calculations	145
7.4 Results and Discussion	148

*1 Presented before at the General Discussion on Molecular
Structure held at Hokkaido Univ., Oct. 1967.

7.1 Summary

Simple molecular orbital calculation of the enolate ion of 3-substituted-2,4-pentanediones has been made for the purpose of evaluating the electronic effect of 3-substituents. The decrease of electron density on the enol oxygen results in the shift of the enol proton toward the lower magnetic field in the nmr spectra.

The π -electron structure of β -dicarbonyls such as acetylacetone, benzoylacetone, dibenzoylmethane and β -keto esters have been investigated in the semiempirical SCF-LCAO-MO approximation. The comparison of the bond order and electron density showed relatively good agreement with observed infrared spectra.

7.2 Introduction

Several investigations on the electronic structure of enolate ion¹⁻³ have been reported. Although there are somewhat difference, the electronic structure and π - π^* transition absorption have been reasonably explained. As far concerned with intramolecular hydrogen bond, the most important problem is whether vacant 2p-orbital of hydrogen perpendicular to the chelate ring, can participate in π -electron system of the chelate ring. Preliminary extended Hückel MO treatment by Morokuma et al⁴ suggested the less possibility of the participation of 2p-orbital perpendicular to the chelate ring. To the

contrary, Shigorin⁵ has stated that construction of quasi aromatic ring can be performed by taking account of 2p π -orbital of hydrogen associated with hydrogen bonding using SCF-LCAO-MO calculation.⁶ This conclusion seems to give us easier understanding to peculiar phenomena of the chelate ring. However, the validity of the MO calculation is still suspicious because of the high promotion energy from 1s orbital to 2p orbital of hydrogen atom. Therefore, more advanced treatment will be required to describe the nature of hydrogen bond of the complex molecule.

Since intramolecular hydrogen bond is strongly associated with the π -electron system, molecular orbital calculation in Hückel and Self consistent field approximation have been carried out in order to interpret the properties of enolate ion of β -dicarbonyls neglecting hydrogen bonded system.

7.3 The Procedure of Calculations

A. Hückel Molecular Orbital Calculation

A semi-empirical molecular orbital (MO-LCAO) method has been used neglecting overlap integral.⁷ In Hückel method the normalized molecular orbitals are of the LCAO form.

$$\phi_i = \sum_p c_{ip} x_p \quad (1)$$

where the summation index p extendeds over all the atoms in π -electron system. The coefficient, c_{ip} , and orbital energy ϵ_i are determined by diagonalization the H matrix, with elements defined as

$$H_{pq} = \int \chi_p^* H^{\text{eff}} \chi_q d\tau \quad (2)$$

The coulomb integrals $H_{pp} = \alpha_p$ and the resonance integrals, $H_{pq} = \beta_{pq}$ are determined empirically. Although there are some uncertainties in chose of parameters, a set of parameters proposed by Pallman and Pullman⁸ is used in this works. The parameters including hetero atom are evaluated according to Streitwieser.⁷ The hyperconjugative effect of methyl has been considered in the present work.

$$\alpha_{=O} = \alpha_C + 1.2\beta_{CC}$$

$$\alpha_{-O-} = \alpha_C + 2\beta_{CC}$$

$$\beta_{C=O} = 2\beta_{CC}$$

$$\beta_{-O-} = 0.9\beta_{CC}$$

B. SCF-LCAO-MO

The calculation involved the iteration of the solutions of the eigenvalue problem of the matrix F ,

$$F_{i,i}^{(1)} = -I_i + 1/2P_{i,i}^{(0)}(I_i - E_i) + \sum_{i \neq j} (P_{j,j}^{(0)} - Z_j)\gamma_{i,j} \dots$$

..... (3)

$$F_{i,j} = \beta_{i,j} - 1/2 P_{i,j}^{(0)} \gamma_{i,j}$$

The index is the same as that used by Pople.⁹ The Coulomb integrals have been evaluated according to approximation proposed by Mataga and Nishimoto.¹⁰

$$\gamma_{i,j} = e^2 / (R_{i,j} + a_{i,j}) \quad (4)$$

The molecular dimension in this calculation were quoted from crystallographic result by Williams.¹¹ The constants $a_{i,j}$ are defined by the following expression.

$$\gamma_{i,i} = e^2 / a_{i,i} = I_i - E_i \quad (5)$$

$$e^2 / a_{i,j} = 1/2 (I_i - E_i + I_j - E_j) \quad (6)$$

I_i and E_i indicate the ionization potential and electron affinity of the i -th atom in valence state respectively.¹²

The parameters used in this work are

$$\begin{array}{lll} I_{=O} = 17.70 \text{ eV} & E_{=O} = 2.47 \text{ eV} & \beta_{C-C} = -2.56 \text{ eV} \\ I_{-O-} = 27.60 \text{ eV} & E_{-O-} = 4.94 \text{ eV} & \beta_{C=O} = -2.39 \text{ eV} \\ I_C = 11.16 \text{ eV} & E_C = 0.03 \text{ eV} & \beta_{C-O-} = -1.33 \text{ eV} \end{array}$$

All calculations have been carried out using a digital computer Model KDC-II at Kyoto University. The iteration were continued until the difference of each coefficient of atomic orbital at i th step and that of $i + 1$ the step converged within 0.001.

7.4 Results and Discussion

The Hückel MO calculations have been carried out for acetylacetone, 3-chloro, 3-propenyl, 3-cyano, 3-nitro and 3-acetyl-2,4-pentanedione.

Figure 1 demonstrates the plot of the chemical shift of enolic proton against the π -electron charge density on enolic oxygen. The linear relationship between them indicates that the lower electron density on the enolic oxygen causes the lower magnetic field shift of the enolic proton. A contribution of ionic structure of enol form at the ground state seems to have profound effect on the intramolecular hydrogen bond. Although an alternative explanation using vacant 2p-orbitals of hydrogen may be possible in the same way as in mono substituted benzene, this concept is not necessary to interpret this system. One may suppose that the expansion to 2p-orbital in Lithium must be much easier than that of hydrogen atom. However, recent report has suggested that the contribution of 2p π -orbital of Lithium in acetylacetonate is proved to be negligible by vibrational spectra.¹³

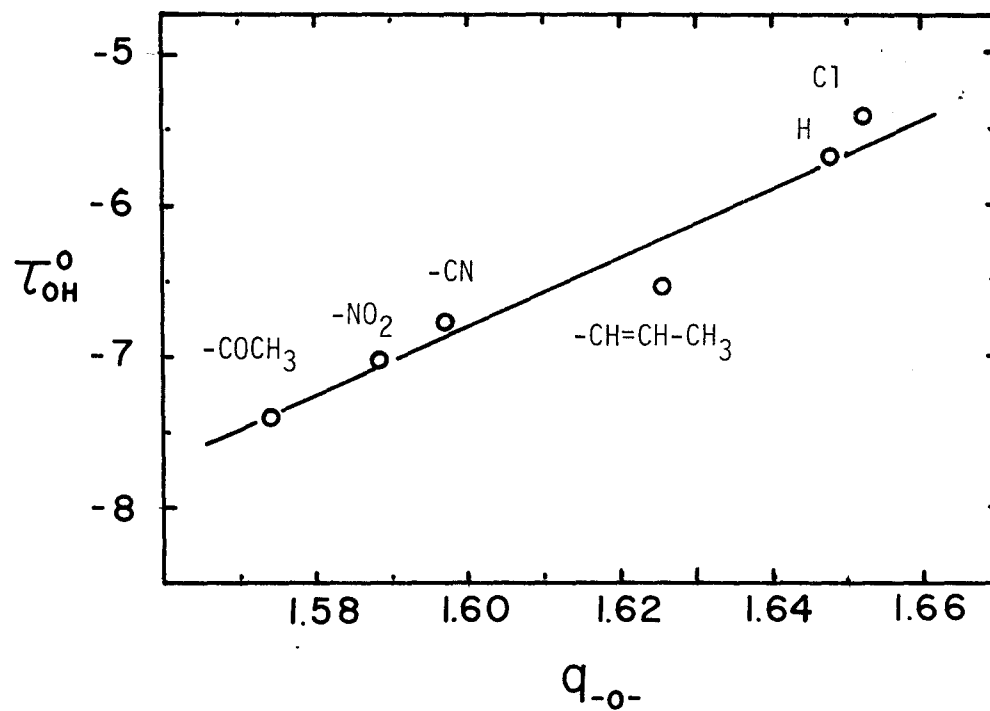
Figure 2 and 3 illustrate the π -electron charge density and bond order resulted from self consistent field approximation. Comparison of bond order of C=C and C=O with the stretching vibration shows parallelism as is seen in Table 1. Two vibrations are obviously distinguished for β -keto ester. However, two

vibrations are superimposed in the spectra of the enol structure of β -dicarbonyls which used to be splitted into two absorptions upon deuteration of enol proton. These frequencies must be interpreted with the both bond orders of C=C, and C=O, because the superimposition of the two bands gives rather vague measure to evaluate the results of calculation. Delocalization of π -electron appears to have some relation with the strength of hydrogen bond owing to the resultant electronic effect and the deformation of the structure of the chelate ring whose molecular dimension is fixed in calculations. More advanced calculation involving σ -orbitals should be required to do elaborate discussions.

Table 1. Bond order and observed frequencies of (C=O) and (C=C)

	Bond order			Obs. freq. (cm^{-1})	
	P(C=O)	P(C=C)	P(C=O)+P(C=C)/2	$\nu(\text{C=O})$,	$\nu(\text{C=C})$
β -keto ester	0.894	0.782	0.838	1650	1632
acetylacetone	0.803	0.732	0.768	1618	
benzoylacetone	0.802	0.698	0.750	1605	
dibenzoylmethane	0.766	0.704	0.735	1600	

Fig. 1 Correlation of chemical shifts of enol proton
with electron densities at enol oxygen



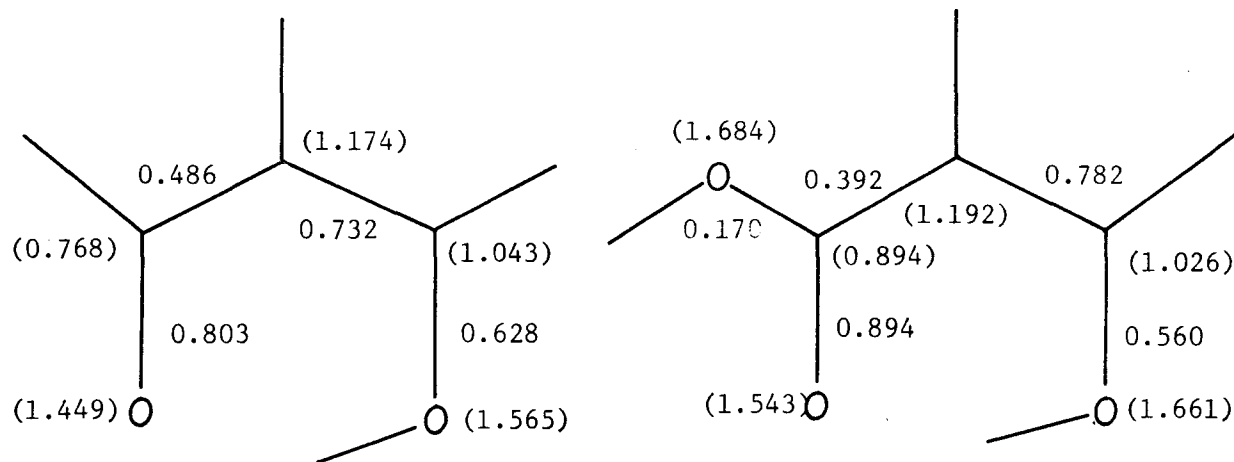


Figure 2 Charge density (in parenthesis) and bond-order of enolate ion of acetylacetone and β -ketoester

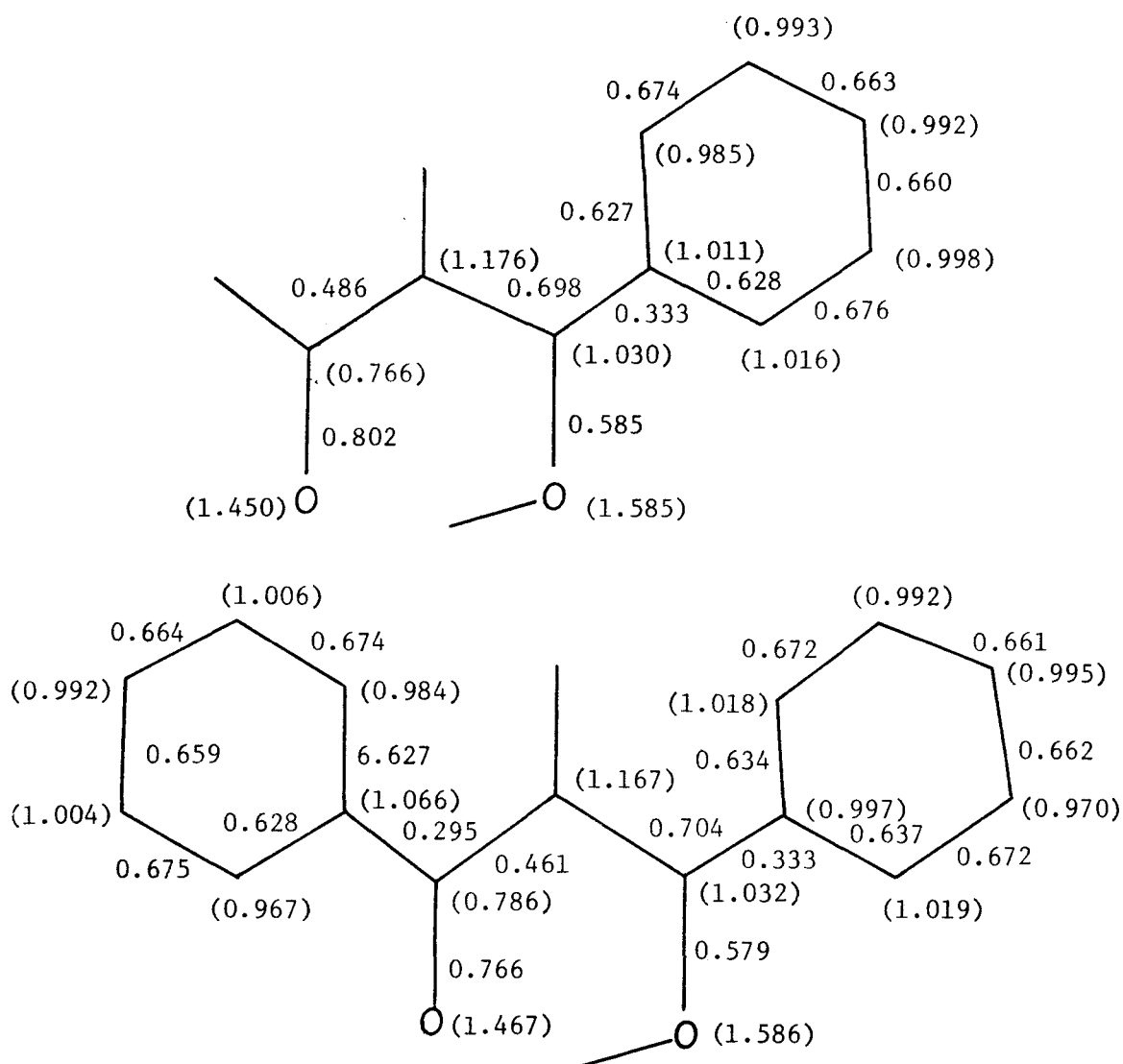


Figure 3 Charge density (in parenthesis) and bond-order of enolate ion of benzoylacetone and dibenzoylmethane

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Chapter 8

The Theory and Application of Normal Coordinate Analysis: ^{*1}	
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^{*1} Presented before at the General Discussion on Molecular
Structure held at Tokyo, Oct., 1968.

Introduction

Chemist have studied the vibrational spectra of the complex molecules to obtain information about their chemical structures. They have assigned the observed frequencies to a particular group frequency and related the differences in group frequencies between structurally connected molecules to difference in chemical structure. An emprical method is reasonable, only if the vibrational mode of particular group is less coupplred with the motion of the rest of the molecule.

Therefore, they have unconsciously made band assignments of the observed frequencies according to the concept of the group frequency.

However, theory indicates that all atoms of molecule in normal vibration perform their harmonic oscillations. Consequently a pure isolated vibration, that is just as diatomic vibration, can not be expected for polyatomic molecules.

Invalidity of empirical approach can be shown in the cases:
(1) In cyclic molecules, some vibrations couple with another vibrations as a result of the trigonometric requirements of a ring structure. (2) Generally, vibrational coupling can happen when two groups vibrations show the close frequencies to each

other. The strong coupling is usually observed in the stretching vibrations of adjacent bonds which consist of atoms of similar masses and are of approximately equal strength.

Extreme care must be paid in interpreting the observed frequencies owing to the vibrational coupling. Empirical approach can not assure chemist whether the observed differences are attributed to the changes in chemical bonding or resultant coupling.

Thus the theoretical analysis of vibrational spectra can be handled by normal coordinate analysis which gives a set of force constants to express the inter-atomic forces in a molecule. One may interpret the chemical structure of a molecule in terms of a set of force constants. A brief description of the theoretical treatment of normal vibration (normal coordinate analysis) and the outline of program to execute this calculation.

8.1. Normal vibrations and Normal coordinates

In diatomic molecule, vibration occurs along the line connected with two nuclei. Complicated vibration seems to be expected in polyatomic molecule because each atom vibrates as a harmonic oscillator.

The kinetic energy of N-atom is given by

$$2T = \sum_N m_N \left[\left(\frac{d\Delta x_N}{dt} \right)^2 + \left(\frac{d\Delta y_N}{dt} \right)^2 + \left(\frac{d\Delta z_N}{dt} \right)^2 \right] \quad (1)$$

where Δx_N , Δy_N , and Δz_N represent small displacement of the N-th atom from its equilibrium position along the x, y, and z axes. respectively.

The cartitian coordinates are transfered its mass-weighted coordinates q_1, q_2 , and q_3 .

$$\left. \begin{aligned} q_1 &= \sqrt{m_1} \cdot \Delta x_1 \\ q_2 &= \sqrt{m_1} \cdot \Delta y_1 \\ q_3 &= \sqrt{m_1} \cdot \Delta z_1 \end{aligned} \right\} \dots\dots\dots (2)$$

The kinetic energy will be expressed in

$$2T = \sum_i^{3N} \dot{q}_i^2 \dots\dots\dots (3)$$

For potential energy , it may be expanded in a Taylor's series as

$$\begin{aligned} V(q_1, q_2, \dots, q_{3N}) &= V_0 + \sum_i^{3N} \left(\frac{\partial V}{\partial q_i} \right)_0 \cdot q_i \\ &+ \frac{1}{2} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots\dots\dots \end{aligned} \quad (4)$$

The $(\partial V / \partial q_i)_0$ equals to zero since V must be a minimum at $q_i=0$.

$$V = \frac{1}{2} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i \cdot q_j = \frac{1}{2} \sum_{i,j}^{3N} b_{ij} \cdot q_i \cdot q_j \dots\dots\dots (5)$$

Substitution of the expressions for kinetic and potential energies into Newton's equation of motion,

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_i} \right) + \frac{\partial V}{\partial q_i} = 0 \quad i = 1, 2, \dots, 3N, \quad (6)$$

yields a set of 3N simultaneous linear differential equations,

$$\ddot{q}_i + \sum_j b_{ij} \dot{q}_j = 0 \quad j = 1, 2, \dots, 3N \quad (7)$$

A solution is

$$q_i = q_i \cdot \sin(\sqrt{b_{ij}} t + \delta_i) \quad (8)$$

Generally speaking, the coordinates must be transformed into a new set of coordinates which are termed normal coordinates.

They are defined by

$$Q_k = \sum_{i=1}^{3N} l'_{ki} q_i \quad k = 1, 2, \dots, 3N \quad (9)$$

which l'_{ki} are chosen so that the kinetic and potential energy may be expressed by the relations,

$$2T = \sum \dot{Q}_k^2 \quad (10)$$

$$2V = \sum \lambda_k \cdot Q_k^2 \quad (11)$$

From equation (6), the following equation is given;

$$\ddot{Q}_k + \lambda_k Q_k = 0 \quad (12)$$

Solution of (12) gives

$$Q_k = Q_k^0 \sin(\sqrt{\lambda_k} kt + \delta_k) \quad (13)$$

which yield the frequency which is called as normal vibration.

$$\nu_k = 1/2\pi \cdot \sqrt{\lambda_k} \quad (14)$$

8.2 The Application of Wilson's Method to Normal Coordinate Analysis.

The Wilson's GF matrix¹ method considerably simplifies the solution of the secular equation. A brief procedure of this method is summarized as following.²

1. Selection of internal coordinates
2. Expression of the potential energy in terms of internal coordinates
3. The B matrix defined by molecular configuration
4. The construction of the G matrix using the B matrix.
5. Application of the group theory to deduce the matrix into the small block matrices
6. Calculation of eigen values and eigen vectors of GF matrix.
7. Determination of frequencies from eigen values and vibrational modes from eigen vectors.

8.3 Urey-Bradley Force Field

The two familiar potential fields are the general force field

(GVF) and the Urey-Bradley force field (UBF). The potential energy expression for the GVF field is given by

$$2V = \sum_i f_{r_i} (\Delta r_i)^2 + \sum_{i,j} f_{r_i r_j} (\Delta r_i)(\Delta r_j) + \sum_{i \neq j} f_{\alpha_{ij}} (r_{ij} \Delta \alpha_{ij})^2 \\ + \sum_{i,j,k} f_{r_i \alpha_{jk}} (\Delta r_i)(\Delta r_{jk} \Delta \alpha_{jk}) + \sum_{i \neq j, k \neq l} f_{\alpha_{ij} \alpha_{kl}} (r_{ij} \Delta \alpha_{ij}) \cdot (r_{kl} \Delta \alpha_{kl}) \quad (15)$$

where f_{r_i} and $f_{\alpha_{ij}}$ denote the stretching force constant of the bond, whose length is r_i and the bending force constant of the α_{ij} angle, respectively. $f_{r_i r_j}$, $f_{r_i \alpha_{jk}}$ and $f_{\alpha_{ij} \alpha_{kl}}$ indicate the interaction force constants between stretching and stretching coordinates, between stretching and bending coordinate, and between bending and bending coordinate.

In UBF field, the repulsion between the non-bonded atoms is taken account into the potential. The general expression of the UBF is expressed by

$$2V = \sum_i \left[K_i (\Delta r_i)^2 + 2K'_i r_i (\Delta r_i) \right] + \sum_{i \neq j} \left[H_{ij} (r_{ij} \Delta \alpha_{ij})^2 + 2H'_{ij} r_{ij} (r_{ij} \Delta \alpha_{ij}) \right] + \sum_{i \neq j} \left[F_{ij} (\Delta q_{ij})^2 + 2F'_{ij} q_{ij} (\Delta q_{ij}) \right] \quad (16)$$

K_i , H_{ij} , and F_{ij} represent stretching, bending and repulsive force constants, respectively. q_{ij} is the distance between the two non-bonded atoms i and j . Geometrical restriction is related by

$$q_{ij} = (r_i^2 + r_j^2 - 2r_i r_j \cos \alpha)^{1/2} \quad (17)$$

8.4 Principle of Normal Coordinate Analysis

The number of normal vibrations for N-atom molecule is $3N-6$ for non-linear molecule and $3N-5$ for linear molecule. Among normal vibrations, infra and Raman active species are determined by the selection rule using the group theory.

The kinetic energy is expressed by $3N$ cartesian coordinates.

$$T = \frac{1}{2} m_1 \dot{x}_1^2 + \frac{1}{2} m_1 \dot{y}_1^2 + \frac{1}{2} m_1 \dot{z}_1^2 + \cdots + \frac{1}{2} m_N \dot{x}_N^2 + \frac{1}{2} m_N \dot{y}_N^2 + \frac{1}{2} m_N \dot{z}_N^2 \quad \text{----- (18)}$$

Above equation is simplified using matrix and vectors.

$$X = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ x_N \\ y_N \\ z_N \end{pmatrix} \quad M = \begin{vmatrix} m_1 & & & & & & \\ & m_1 & & & & & \\ & & m_1 & & & & \\ & & & \ddots & & & \\ & & & & m_N & & \\ & & & & & m_N & \\ & & & & & & m_N \end{vmatrix} \quad \text{----- (19)}$$

$$2T = X \cdot \tilde{M} X$$

The potential energy is given using the internal coordinates

$$V = \frac{1}{2} R F_R \tilde{R} \quad \text{----- (20)}$$

where

$$R = \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \\ \vdots \\ \Delta \alpha_1 \end{bmatrix} \quad F_R = \begin{vmatrix} f_{11} & f_{12} & \dots & \dots & f_{1n} \\ f_{21} & f_{22} & & & \vdots \\ \vdots & \vdots & & & \vdots \\ f_{n1} & \dots & & \dots & f_{nn} \end{vmatrix}$$

\widetilde{R} denotes its transpose.

The coordinates are transformed to express two energy matrices in the common coordinates.

$$\begin{aligned} X &= U \cdot q \\ R &= U^R \cdot q \end{aligned} \quad \text{----- (21)}$$

In common coordinate, two energy matrices are defined by

$$\begin{aligned} 2T &= \widetilde{q} G^{-1} q \\ 2V &= \widetilde{q} \cdot F \cdot q \end{aligned} \quad \text{----- (22)}$$

The transformation matrix is correlated by

$$\begin{aligned} G^{-1} &= \widetilde{U} \cdot M \cdot U \\ F &= \widetilde{U} \cdot F \cdot U \end{aligned} \quad \text{----- (23)}$$

In order to determine the modes of normal vibrations, it is necessary to calculate the L matrix, defined by

$$q = LQ$$

If the L matrix is obtainable, (23) are transformed into

$$\widetilde{L} G^{-1} L = E \quad \text{----- (24)}$$

$$\widetilde{L} F L = \Lambda \quad \text{----- (25)}$$

E is the unit matrix. Inverse matrix of (24) is written by

$$((\tilde{L}G^{-1})(L))^{-1} = (L^{-1})(\tilde{L}G^{-1})^{-1} = (L^{-1})(G^{-1})^{-1}(\tilde{L})^{-1}$$

$$L^{-1}G(\tilde{L})^{-1} = E \text{ ----- (26)}$$

The multiplication of (25) by (26) gives

$$L^{-1}G(\tilde{L})^{-1}(\tilde{L})FL = EA = \Lambda$$

$$L^{-1}G F L = \Lambda \text{ ----- (27)}$$

(27) multiplied by L from left hand yields

$$LL^{-1} G F L = G F L = \Lambda L \text{ ----- (28)}$$

Therefore, this problem is attributed to solve the secular equation

$$|GF - E \lambda| = 0 \text{ ----- (29)}$$

Consequently the potential energy is expressed by

$$V = \frac{1}{2} \tilde{Q} \tilde{L} F L Q = \frac{1}{2} \tilde{Q} \Lambda Q \text{ ----- (30)}$$

The relation between internal coordinate R and normal coordinates Q is shown by the following equations.

$$\begin{aligned} R_1 &= L_{11}Q_1 + L_{12}Q_2 + \text{-----} + L_{1N}Q_N \\ R_2 &= L_{21}Q_1 + L_{22}Q_2 + \text{-----} + L_{2N}Q_N \\ &\vdots \\ R_i &= L_{i1}Q_1 + L_{i2}Q_2 + \text{-----} L_{iN}Q_N \end{aligned} \text{ ----- (31)}$$

A particular frequency is expressed by

$$\lambda_a = \sum_{i,j} \tilde{L}_{ai} F_{ij} L_{ja} = \sum_{i,j} F_{ij} L_{ia} L_{ja} \text{ ----- (32)}$$

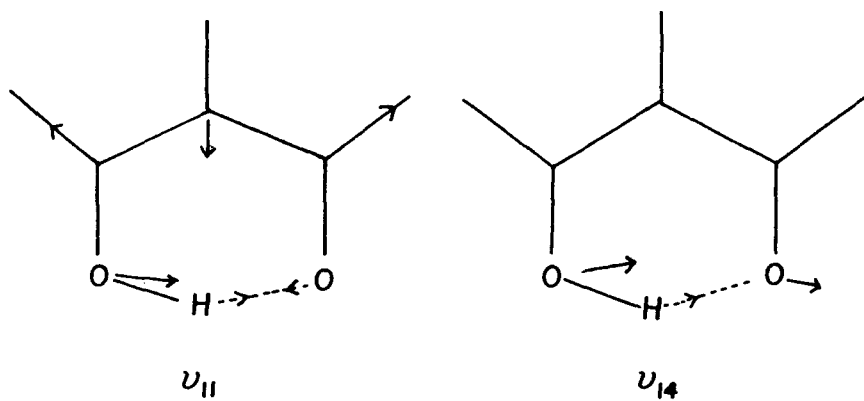
$F_{ij}L_{ia}L_{ja}$ indicates the distribution of the potential energy in each internal coordinate.⁴

8.5 Application of Normal Coordinate Analysis

It is of great interest to compare the electronic effect of sulfur and chlorine at 3-position on the enol form of 2,4-pentanedione, because both atomic weights are not different so much. Therefore, vibrational spectra of 3-methylthio- (I) and 3-chloro-2,4-pentanedione (II) can tell us the difference in their electronic effect.

The whole procedures have been followed as described in Chapter II. The infrared spectra of (I), (II), and their deuterio analogs are shown in Fig. 1 and Fig. 2. The set of force constants are listed in Table 1, 2 and 3. Table 4 illustrates band assignments according to the potential energy distributions. The comparison of stretching force constants of (I) and (II) is demonstrated in Fig. 3.

As is seen in Table 4, the two frequencies ν_1 and ν_2 are easily explained by high percentages of contribution of coordinates S_1 and S_2 . However, it is evidently indicated that the rest of thirteen frequencies consist of more than two vibrational modes expressed in internal coordinates. For instance, hydrogen bonded stretching contribute to ν_{11} , 452 cm^{-1} and ν_{14} , 225 cm^{-1} which vibrational modes are schematically expressed as follow



Comparison of the force constants of (I) and (II) shows a fair agreement with the result of nmr spectra. (I) forms more stronger hydrogen bond than that of (II).

Table 1 Force Constants of 3-chloro- and 3-methylthio-
2,4-pentanedione. (in millidynes per angstrom).

	Stretching	
	X=S	X=Cl
K(C-O)	6.300	5.100
K(C=O)	8.000	8.300
K(C=C)	4.800	5.000
K(C-C)	4.600	4.700
K(C-R)	3.800	4.000
K(C-R')	4.000	4.100
K(O-H)	3.500	3.950
K(O·····H)	0.400	0.300
K(C-X)	2.500	2.150

Table II		
Bending		
H(C=C-O ₁)	0.200	0.200
H(R-C=C)	0.250	0.250
H(R-C-O ₁)	0.330	0.300
H(O ₂ =C-C)	0.200	0.200
H(R'-C-C)	0.230	0.230
H(R'-C=O ₂)	0.180	0.200
H(C=C-C)	0.300	0.310
H(C=C-X)	0.290	0.280
H(C-C-X)	0.200	0.200
H(C-O ₁ -H)	0.560	0.530
H(C=O ₂ ·····H)	0.220	0.200
H(O ₁ -H·····O ₂)	0.050	0.050

Table III

	Repulsive	
	X=S	X=C1
F(O ₁ ...C)	0.350	0.300
F(R...C)	0.300	0.250
F(R...O ₁)	0.200	0.350
F(O ₂ ...C)	0.350	0.350
F(R...C)	0.300	0.300
F(R' ₁ ...O ₂)	0.150	0.160
F(C...C)	0.250	0.250
F(C...X)	0.360	0.330
F(C...X)	0.350	0.330
F(C...H)	0.250	0.250
F(H...C)	0.150	0.150
F(O ₁ ...O ₂)	0.010	0.010

Table 4

Comparisons of observed and calculated
frequencies of 3-methylthio-2,4-pentanedione

Obs.	Calc. (A')	P.E.D. (%)
2975		
2925		
2915		
2580	ν_1 2744	$s_1(100)$
1576	ν_2 1593	$s_2(73)$
	ν_3 1554	$s_3(29), s_6(14)$
	ν_4 1480	$s_4(28), s_8(21)$
1410	ν_5 1404	$s_5(55), s_3(30)$
1369		
1314		
1255	ν_6 1217	$s_6(42), s_3(29)$
1060		
1017		
992		
966		
905	ν_7 904	$s_7(58), s_8(16), s_9(30)$
	ν_8 897	$s_8(50), s_7(31)$
701		
654		
634	ν_9 630	$s_9(34), s_{11}(32)$
563	ν_{10} 568	$s_{10}(53),$
536		
452	ν_{11} 439	$s_{11}(40), s_{14}(23)$
398	ν_{12} 383	$s_{12}(36), s_{11}(41)$
270	ν_{13} 291	$s_{13}(37), s_{12}(26)$
225	ν_{14} 220	$s_{14}(35), s_{13}(25)$
205	ν_{15} 202	$s_{15}(40), s_{13}(45)$

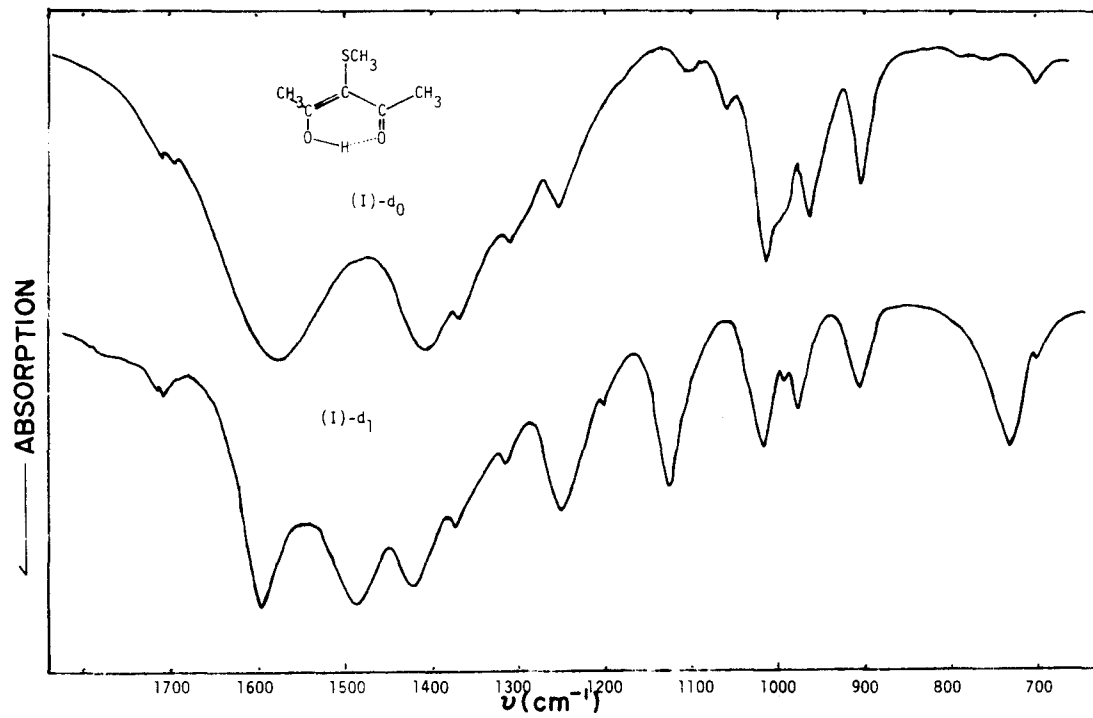


Fig. 1. Infrared spectra of 3-methylthio-2,4-pentanedione (I) and deuterio analog.

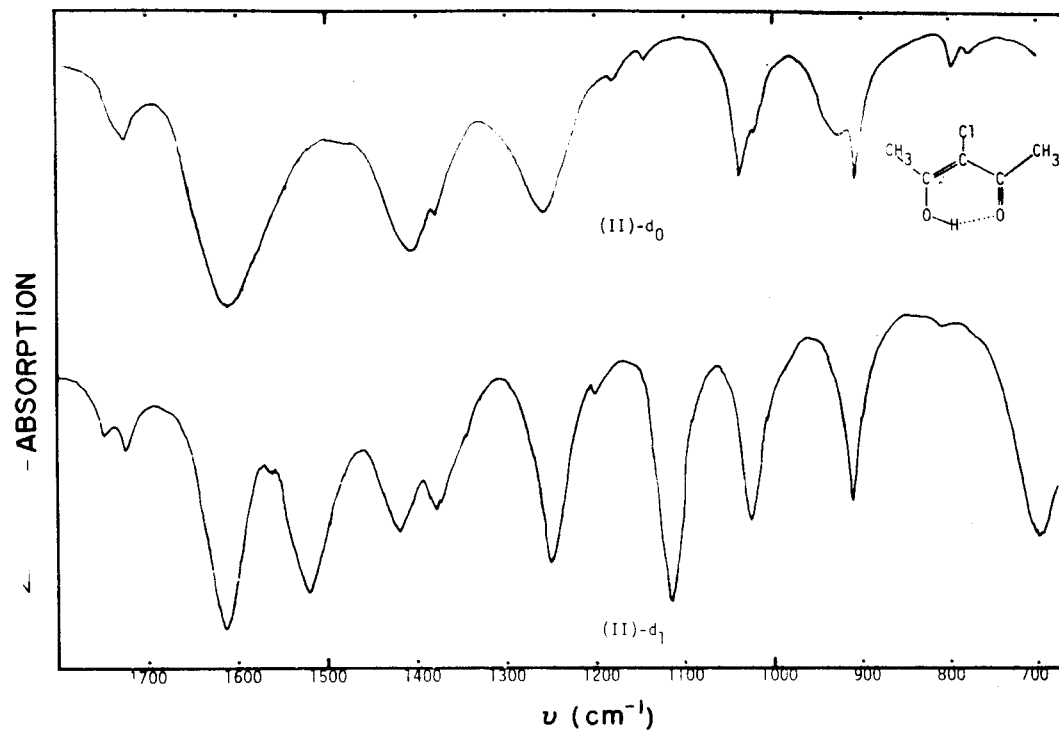
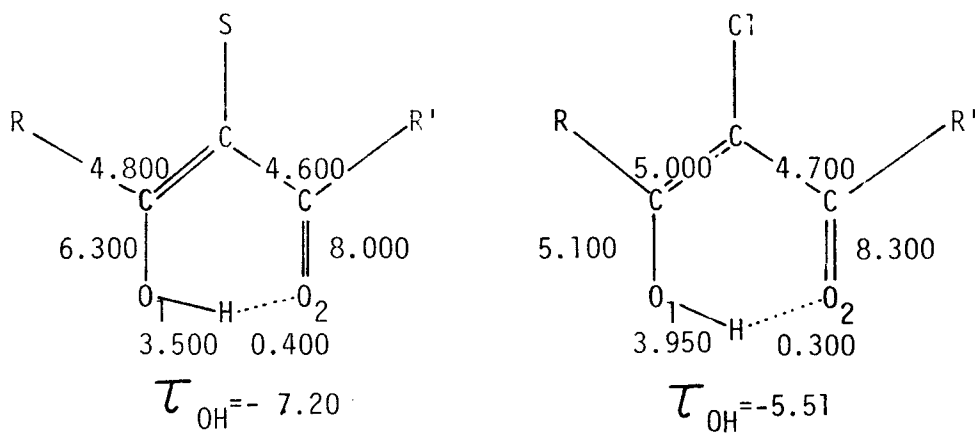


Fig. 2. Infrared spectra of 3-chloro-2,4-pentanedione (II) and deuterio analog.

Fig. 3 Comparison of stretching force constants



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Appendix

Flow Diagram of Computational Calculations

It has been recognized that the high speed digital computer facilitates the tedious and complicated calculations in the field of the chemistry. They include the solution of secular equation in quantum chemistry and normal coordinate analysis, and the coupling problem in nmr spectrum. Especially, the analysis of three dimensional Fourier Series by computer affords a considerably powerful tool to elucidate the molecular structure. Furthermore, complicated reaction rate expressed in linear differential is also solved using Runge-Kutta-Gill method in computer.

In this work, programs have been developed to carry out molecular orbital calculations and normal coordinate analysis. Normal vibrations can be calculated by three main programs; G-program is intended to construct the G elements and sort into the groups according to the molecular symmetry. F-program provides the F elements based on Urey-Bradley force field. Final program is used in order to solve higher order secular equation giving eigen value and eigen vector, from which the frequencies and potential energy are obtained. The brief flow diagram of the third program is shown in Figure 1. A flow diagram illustrated in Figure 2 represents the program for SCF-LCAO-MO calculation, where the result of Hückel MO calculation is given at the first step of interactive calculation. All statements in program are

written according to the FORTRAN IV system.

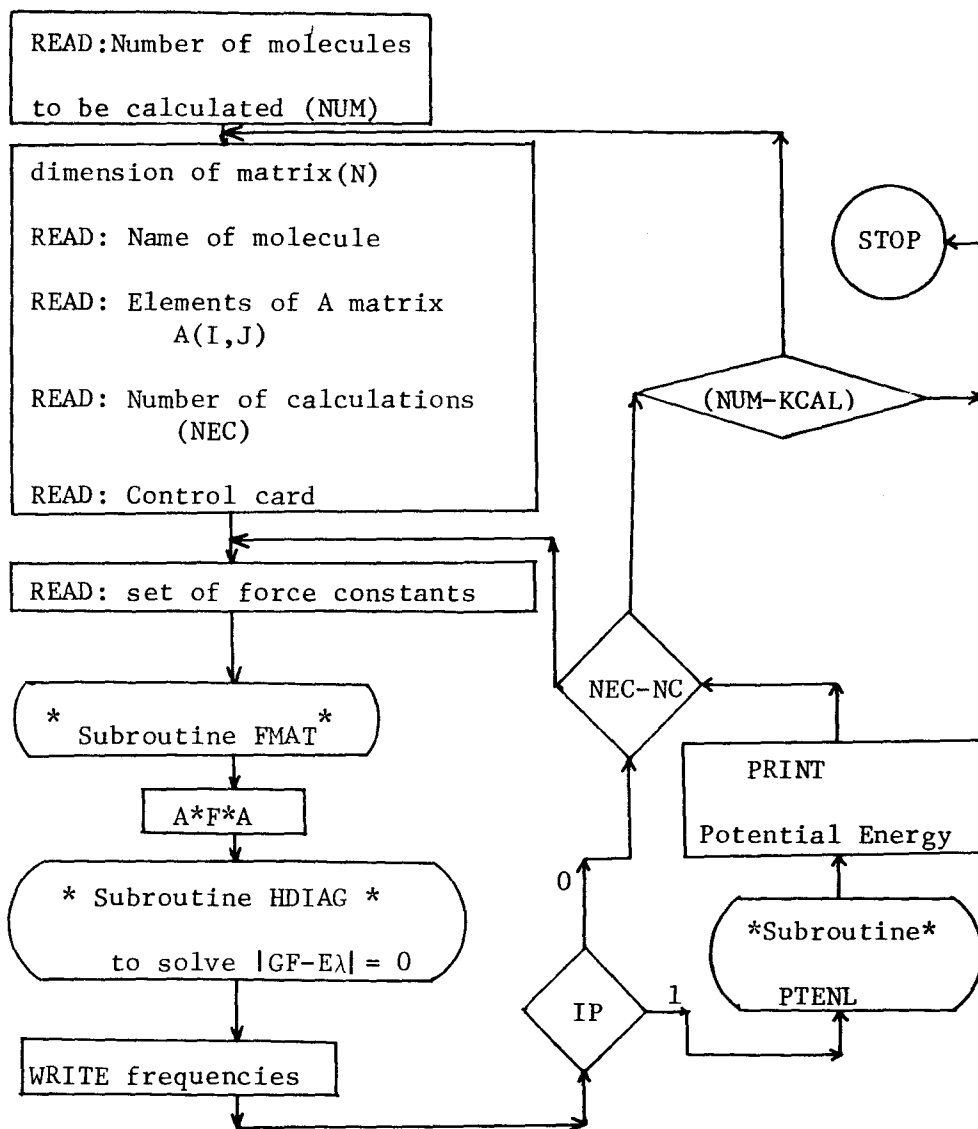


Fig. 1. Block diagram to obtain frequencies and potential energy distribution.

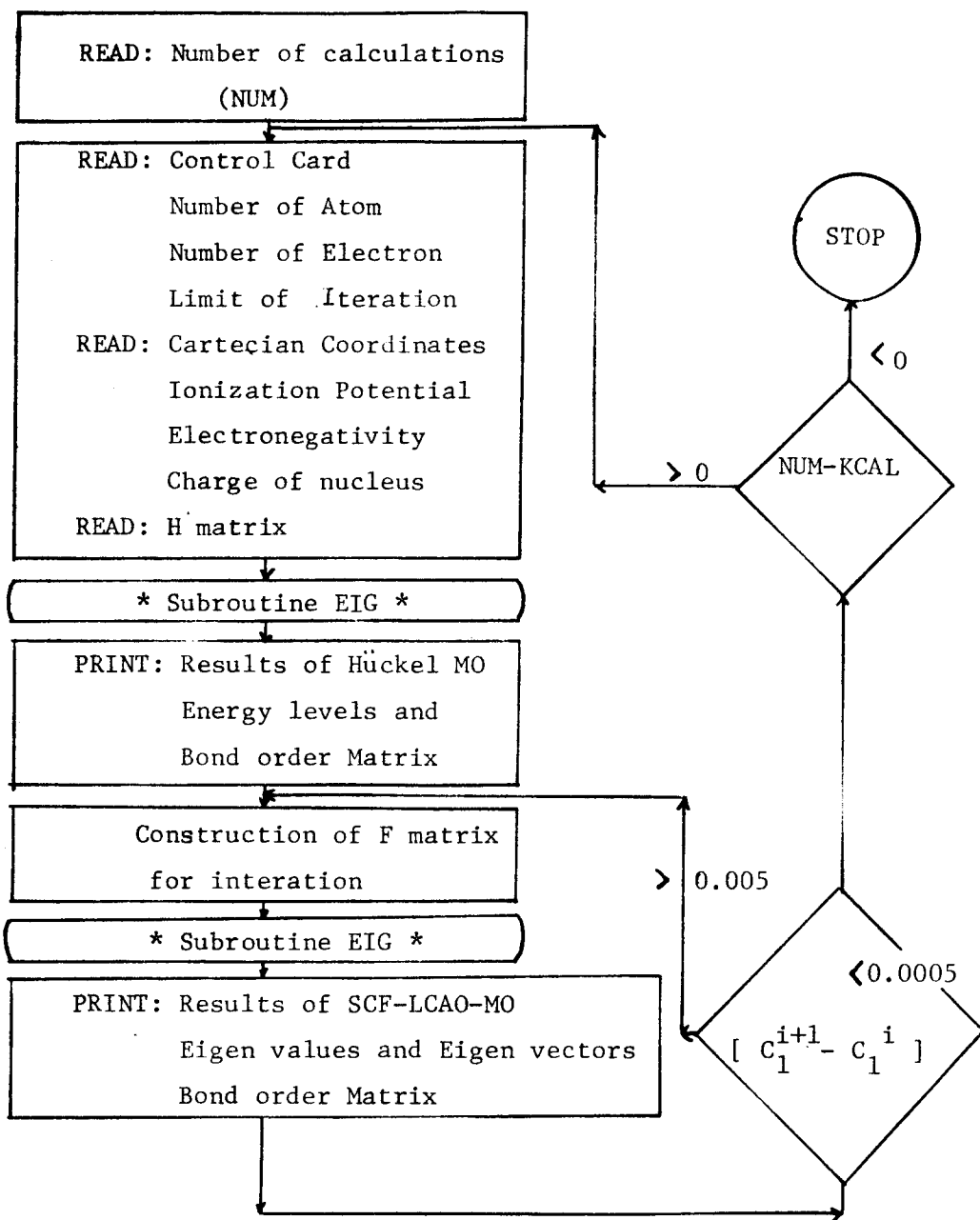


Fig. 2. Block diagram for Huckel and SCF-LCAO-MO